SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
Vol. 33, No. 8, pp. 1459–1468, 2003

Heterobimetallic Complexes Containing Cu and Si

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ABSTRACT

[Bis(propanediamine)Cu]Cl_2, (**1**) was allowed to react with $SiCl_4$ to yield a bimetallic complex (**2**). Compound (**2**) was then treated with pyridine to attain the maximum coordination number of silicon (**3**). The reaction was also followed conductometrically. Complex (**3**) was reacted with sodium diethyl dithiocarbamate (dtc) to yield (**4**). The dtc in (**4**) acts as a bidentate chelating agent as its IR spectrum showed the CS_2 stretching frequency at 1020 cm^{-1} which is characteristic of a symmetrically bonded dithiocarbamate group. There is a common peak in the range 246 to 260 nm in the UV-Vis. spectra of (**1**), (**2**) and (**3**) due to $L \rightarrow M$ charge transfer. The EPR spectra of all species showed different environments for the Cu(II) ion in the various compounds indicating stereochemical changes.

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DOI: 10.1081/SIM-120024322
0094-5714 (Print); 1532-2440 (Online)

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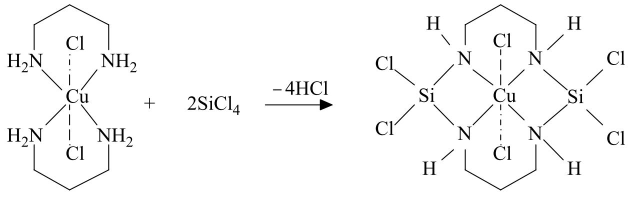
INTRODUCTION

In recent years, studies of heteronuclear bimetallic complexes have been of increasing importance in inorganic and bioinorganic chemistry.[1–5] In this communication an attempt has been made to synthesize a trinuclear compound containing three metal atoms and also to study their reactions.

RESULTS AND DISCUSSION

Analytical data, melting points and molar conductance of the compounds are given in Table 1. The conductometric titration of $CuCl_2$ with 1,3-propanediamine (ppn) in ethanol was done at ambient temperature and indicated the formation of a 1:2 compound (Figure 1). Further addition of Cu(II) ion into the propanediamine solution showed an increase in conductance which then became almost constant due to the increase in Cu(II) ion concentration, however, precipitation did not occur owing to very low concentration of the reacting components. The molar conductance of a one millimolar solution of the compound (**1**) in DMSO showed it (Table 1) to be a 1:1 electrolyte as has been noted for potassium thiocyanate[6] in DMSO.

Compound (**1**) was allowed to react with $SiCl_4$ according to Eq. 1 resulting in the formation of a trinuclear compound containing one copper and two silicon atoms (**2**). Since Group IV elements have the capability to extend their coordination number from 4 to 6, pyridine was added to compound (**2**) to achieve a coordination number 6 at silicon, Eq. 2. Since Cu(II) is centrally placed in (**2**) and, being a non-linear molecular system, it will undergo some type of distortion which would lower the symmetry. Thus, a weakly held Cu(II) ion would have a distorted octahedral geometry.



(**1**) (**2**) (1)

Table 1. Analytical data and molar conductance of complexes.

Complex (FW)	Color	M.p. (°C)	Yield (%)	Analysis, found (calcd),%					Molar conductance ohm^{-1} cm^{2} mol^{-1}	
				C	H	N	Cl	S	DMSO	DMF
(**1**) $C_6H_{20}Cl_2CuN_4$ (282.5)	Blue	218	51	24.95 (25.48)	7.33 (7.07)	19.35 (19.81)	25.63 (25.13)	-	42	-
(**2**) $C_6H_{16}Cl_6CuN_4Si_2$ (476.5)	Yellow	260	63	17.31 (17.75)	4.32 (3.94)	14.13 (13.81)	44.21 (44.70)	-	88	-
(**3**) $C_{26}H_{36}Cl_6CuN_8Si_2$ (729.5)	Blue	275	49	43.62 (43.24)	5.45 (4.98)	15.92 (15.52)	26.54 (26.87)	-	-	54
(**4**) $C_{10}H_{16}CuN_8S_8Si_2$ (701.0)	Yellow	> 360	52	8.70 (19.22)	2.90 (2.56)	18.40 (17.94)	–	36.08 (36.58)	-	85

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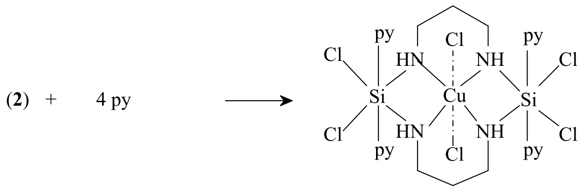
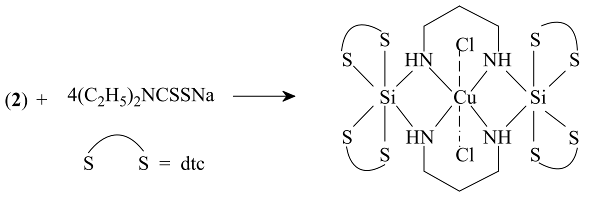


(**3**)

(2)



(**4**)

(3)

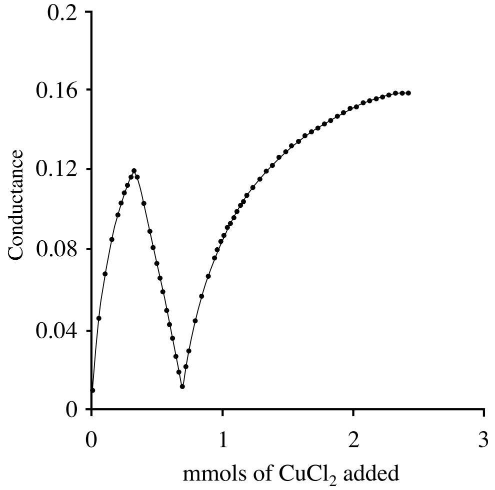


Figure 1. Plot of conductometric titration of 0.5 mmol of ppn (dissolved in 10 mL ethanol) with $CuCl_2$ in mmols (0.05 molar solution in ethanol).

The reaction of (**2**) with pyridine was followed conductometrically at room temperature. When a pyridine solution was added to a solution of the same concentration of (**2**), the molar conductance fell sharply until four moles of pyridine have been added and then became almost constant. Further addition of pyridine did not show any change in the conductance because pyridine is a non-conducting species. The molar conductance of a one millimolar solution of compound (**3**) was also measured at room temperature in DMF (Table 1). The value suggested that compound (**3**) is a 1:1 electrolyte similar to $(CH_3)_4NI$ for which the molar conductance in DMF[6] is 88 $ohm^{-1}cm^2\ mol^{-1}$. In an attempt to check if the chlorines in (**2**) are replaceable and if they may undergo substitution reactions, (**2**) was allowed to react with dtc which replaced the chlorine attached to silicon Eq. 3 and yielded compound (**4**). It is to be noted that the coordination number of silicon is thus raised to six.

The formation of compound (**4**) was also followed conductometrically (Figure 2). A sodium diethyl dithiocarbamate solution in ethanol was added to compound (**2**) in DMSO. The conductivity showed an increase until four moles of dtc were added and then became almost constant. The molar conductance of compound (**4**) increases with further addition of dtc as a consequence of the replacement of chlorine by dtc. The molar conductance of a one millimolar solution of compound (**4**) in DMF indicated that it is a 1:1 electrolyte[6] (Table 1).

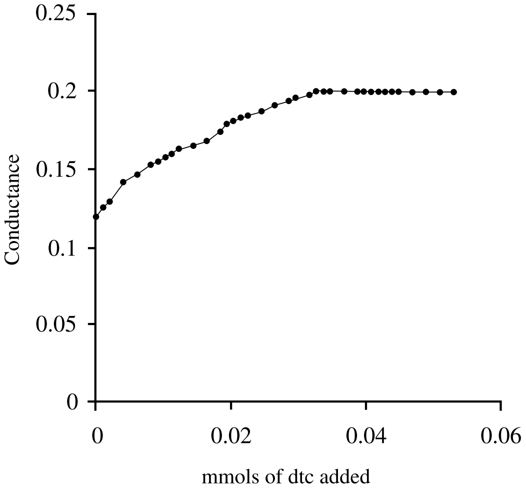


Figure 2. Plot of conductometric titration of 0.01 mmol of compound (**2**) (dissolved in 10 mL DMSO) with dtc in mmols (0.002 molar solution in ethanol).

IR Spectra

The IR spectrum of the primary amine shows two N–H stretching frequencies in the range 3300–3500 cm^{-1} attributed to symmetric and asymmetric modes which are shifted to lower frequency by chelation[7] (Table 2). In compound (**1**) there are two sharp bands at 3222 cm^{-1} (asymmetric) and 3352 cm^{-1}(symmetric), which are due to chelation of copper with ppn. However, a weak band at about 3430 cm^{-1} has also been observed. The N–H deformation band appearing at 1586 cm^{-1} as a sharp band is followed by a shoulder at 1657 cm^{-1}. The other sharp bands in the range 900–650 cm^{-1} are generally due to C–H absorption, which are weakened due to hydrogen bonding. A band appearing at 1213 cm^{-1} has been assigned to ν(C–N).

In compound (**2**) the two ν(N–H) bands (3082 and 3424 cm^{-1}) and two δ(N–H) deformation bands (1482 and 1582 cm^{-1}) have been found to be shifted to lower wave numbers. This decrease is due to the replacement of hydrogen from NH_2 by silicon [Eq. 1]. A band also appears at 1185 cm^{-1}, which is due to the C–N stretching frequency.

When pyridine was added to compound (**2**), the ν(N–H) frequency appears as a broad band at 3431 cm^{-1} followed by a sharp, medium band at 3040 cm^{-1}, which is split into three bands. There is a common band in the 1657–1582 cm^{-1} region in compounds (**1**), (**2**), (**3**) and (**4**). This is a characteristic band of primary amines, which persists in all the complexes. Three C=C and C=N absorption bands are known to appear in the 1580–1485 cm^{-1} range in free pyridine[7] which have been found to be slightly shifted towards lower wave numbers in compound (**3**) due to coordination to silicon. Ring vibrations due to C–H deformation show two bands in the range 1000–1200 cm^{-1} in pyridine.[7] The appearance of these two strong

Table 2. IR spectra of the complexes and their assignments (cm^{-1}).

Compounds	ν(N–H)	δ(N–H)	ν(C–N)	ν(C=S)
Primary amines	3500–3300 b	1650–1590 m	1220–1020 s	-
(**1**)	3352 s 3222 s	1586 s	1213 w	-
(**2**)	3080 vw 3424 vw	1582 s	1185 s	-
(**3**)	3431 b 3030 ms	1575 s	1218 ms	-
(**4**)	2984 ms 3395 b	1614 s	1217 s	1020 s

bands at 1152 and 1078 cm^{-1} confirms the presence of pyridine in compound (**3**).

Compound (**4**) results when (**2**) is allowed to react with dtc. Since dtc may act as both a monodentate or a bidentate ligand this may be ascertained by the criteria laid down by Brinkhoff and Grotens based on IR spectroscopy.[8]

The IR spectrum of a bidentate dtc moiety shows only one ν(C=S) band at around 1000 cm^{-1}, but this band is split into two if it acts as a monodentate ligand. The IR spectrum of compound (**4**) showed only one strong band at 1020 cm^{-1} attributed to the bidentate dtc moiety. The other bands are not closely spaced, they are either much below or much above 1000 cm^{-1}. It is, therefore, ascertained that dtc is acting as a bidentate ligand making silicon six-coordinate.

EPR Spectra

The EPR spectrum of compound (**1**) at room temperature gave the values of g_x, g_y, and g_z of 2.194, 2.135 and 2.070, respectively, and g_{av} is 2.132. The structure of compound (**1**) seems to be distorted octahedral where the coordination of chlorine is probably not perpendicular to the plane defined by copper and the four nitrogens of two propanediamines. The axial positions are very much elongated in order to become stable in the solid state. The g values of Cu(II) generally ranges between 2.06 to 2.38, and our g values fall in the above range. The g_{av} calculated has been found to be 2.132 which is also the value generally found for distorted Cu(II) ions.

The compound (**2**) has a single line spectrum with $g = 2.124$. However, a small peak with $g = 2.08$ is shown, the origin of which is not clear although the presence of an impurity cannot be ruled out. Compound (**2**) is further distorted with respect to compound (**1**) because of the introduction of a second metal. From its EPR spectrum the two signals in the EPR spectrum can be interpreted. The bigger signal with $g = 2.08$ corresponds to a complex structure, where the component of g cannot be separated. The weaker signal with $g = 2.08$ is of unknown origin. Alternatively, the larger component may represent $g_{\perp}$ and the smaller one $g_{\|}$. Since $g_{\perp} > g_{\|}$, the ground state of the system is $d_{3x^2 - r^2}$.

Compound (**3**) has parallel and perpendicular components with $g_{\|} = 2.05$, $g_{\perp} = 2.07$ and $g_{av} = 2.06$. There is hyperfine structure also, as seen in the $g_{\|}$ and $g_{\perp}$ components. The average separation between four hyperfine components is only 3.703 Gauss, which indicates the overlap of the electron at the nuclear site. Since $g_{\perp} > g_{\|}$, therefore, the structure is suggested to be tetragonally-distorted.

In compound (**4**) there is a single broad line spectrum with a half width half maximum at 556 Gauss. This indicates fast relaxation of the Cu(II) ions in the complex. The width can be attributed either to exchange interaction or dipolar interaction. But the shape of the spectral line, which is more of Gaussian than Lorenzian shape, indicates dipolar interaction. However, there is a small shoulder in the spectral line with $g = 2.08$, similar to compound (**2**), which is of unknown origin.

Electronic Spectra

The electronic spectra of compounds (**1**), (**2**) and (**3**) showed a peak at 252 nm ($\log \varepsilon = 2.23\ \mathrm{l\ mol^{-1}\ cm^{-1}}$), 247 nm ($\log \varepsilon = 1.21\ \mathrm{l\ mol^{-1}\ cm^{-1}}$) and 262.4 nm ($\log \varepsilon = 3.29\ \mathrm{l\ mol^{-1}\ cm^{-1}}$), respectively, which is ascribed to $L \rightarrow M$ charge transfer. The slight variation in the absorption of compound (**2**) is due to the addition of $SiCl_4$. A slight variation also occurs in the $L \rightarrow M$ absorption band when pyridine was added to compound (**2**). The $L \rightarrow M$ charge transfer band could not be detected in compound (**4**) which might have been obscured due to the replacement of chloride by the bulky dtc moiety.

In compound (**1**), the d–d charge transfer band appears as broad band at 584 nm ($\log \varepsilon = 2.07\ \mathrm{l\ mol^{-1}\ cm^{-1}}$) in the visible region. The same band appears[9] at 970 nm in compound (**2**), at 900 nm in compound (**3**) and at about 1000 nm in compound (**4**). Copper in compound (**1**), (**2**), (**3**) and (**4**) appears to be tetragonally-distorted octahedral which splits the e and t_2 level.

EXPERIMENTAL

Elemental analyses of the complexes were done with a Carlo Erba 1106 analyser. IR spectra were recorded with a Perkin Elmer model 983 spectrophotometer as KBr discs. UV-Vis. spectra were recorded in the 200–1000 nm range in DMF using a Systronics 117 spectrophotometer at room temperature. Conductance measurements were made on a CM 180 Elico conductivity meter. EPR spectra of the solid compound were recorded on a RE-2X Jeol spectrometer fitted with 100 KHz field modulation. Chloride was determined as AgCl gravimetrically. Propanediamine (Fluka), $CuCl_2 \cdot 2H_2O$, pyridine, sodium diethyl dithiocarbamate (E. Merck), $SiCl_4$ (BDH) were used as received. Ethyl alcohol was used after distillation over $CaCl_2$. All other solvents obtained commercially were used without further purification.

Preparation of Compound (1)

$CuCl_2 \cdot 2H_2O$ (10 mmol, 1.70 g) dissolved in ethanol (25 mL) was added to an ethanolic solution (25 mL) of propanediamine (20 mmol, 1.64

mL) at room temperature, which afforded a deep blue needle-like compound. The supernatant was decanted, the crystals washed with ethanol and diethyl ether and dried over $CaCl_2$ under vacuum. The crystals are soluble in ethanol, methanol, propanol, water, and DMSO but could not be crystallized as they become sticky.

Preparation of Compound (2)

To a dry ethanolic solution (25 mL) of compound (**1**) (5 mmol, 1.41 g) was added $SiCl_4$ (10 mmol, 1.14 g) dissolved in CCl_4 (10 mL). The reaction mixture instantaneously yielded a yellow solid, which was filtered and purified by washing with dry CCl_4 and diethyl ether. Since $SiCl_4$ is hygroscopic all manipulation were done in a dry box to prevent access of moisture.

Preparation of Compound (3)

Compound (**2**) (2 mmol, 0.8 g) dissolved in DMSO (25 mL) was added to an ethanolic solution (10 mL) of pyridine (8 mmol, 0.64 mL). The resulting mixture was refluxed on a water bath for 8 to 10 h and left overnight at room temperature to yield a blue, needle-shaped compound. The compound was washed with cold ethanol and dried in vacuo. It was recrystallised from a 1:1 mixture of nitromethane and DMF.

Preparation of Compound (4)

A solution of sodium diethyl dithiocarbamate (8 mmol, 1.8 g) in 25 mL ethanol was slowly added to compound (**2**) (2 mmol, 0.81 g) dissolved in 25 mL DMSO. The reaction mixture immediately yielded a black solid. The supernatant was decanted, the solid was washed thrice with cold ethanol and dried over $CaCl_2$ in a desiccator. The black compound (**4**) turned yellow when dried. It was soluble in DMF.

ACKNOWLEDGMENT

The authors are thankful to Prof. S. H. Afaq, Faculty of Medicine, for recording UV-Vis. spectra, to the Chairman, Department of Chemistry, for providing the necessary research facilities for this project and to Prof. R. J. Singh, Department of Physics, Aligarh Muslim University, Aligarh, for recording the EPR spectra.

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Received December 6, 2001 Referee I: C. H. Yoder
Accepted May 8, 2003 Referee II: J. D. Zubkowski