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New heterotrinuclear complexes containing copper(II) and a group IV metal

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Summary

Heterotrinuclear complexes of the type $[Cu_2(TETA)_2Cl_4M]$ (M = Si, Ge, Sn, Ti and Zr; TETA = triethylene tetramine) have been prepared by direct reaction of $[Cu[TETA)]Cl_2$ with MCl_4 in a 2:1 ratio in MeOH. The compounds have been characterized by elemental analyses, e.s.r., electronic and i.r. spectra, magnetic susceptibility and conductivity measurements. The results indicate that $[Cu(TETA)]Cl_2$ is square planar and ionic, while its heterotrinuclear complexes, $[Cu_2(TETA)_2Cl_4M]$, are covalent with an octahedral environment around the copper(II) ion.

Introduction

Heterobimetallic complexes are of great interest due to their potential importance in catalysis$^{(1)}$ and in organic syntheses$^{(2)}$. Additional interest in such systems also arises because they may be useful models for the phenomenon of strong metal-support interactions observed in heterogeneous catalysis$^{(3)}$. Convenient routes to new heterobimetallic complexes have recently been investigated$^{(4-7)}$.

We have recently reported$^{(8,9)}$ two types of multimetallic complexes of the type $[Cu(TETA)Cl_2MCl_2]$ (M = Si, Ge, Sn, Ti and Zr; TETA = triethylene tetramine) and $[Cu(en)_2Cl_2M_2Cl_4]$ (M = Si, Ge, Sn, Ti and Zr; en = ethylenediamine). As part of our ongoing studies on heterobimetallic complexes synthesis of a novel type of heterotrinuclear complex containing two copper(II) ions and a group IV metal was attempted. This paper considers the synthesis of complexes of the type $[Cu_2(TETA)_2Cl_4M]$.

Experimental

Triethylene tetramine (Koch Light), cupric chloride, $SiCl_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$, $ZrCl_4$(BDH) were used as received. MeOH and DMSO were distilled before use. Microanalyses of the complexes were done by a Carlo Erba Analyser Model 1106. Molar conductance was measured at room temperature on a Digisun electronic conductivity bridge. The i.r. spectra (200–4000 cm^{-1}) were recorded on a Carl Ziess Specord M-80 spectrophotometer in Nujol mulls. Electronic spectra were recorded on a Shimadzu u.v.–vis. recording spectrophotometer, Model 60. The e.p.r. spectrum was recorded on a Bruker Scientific X-band spectrometer (ESP-300) using a 100 KHz field modulation and quartz sample tubes and the values determined calibrated with DPPA powder, $g = 2.0036$. Magnetic susceptibility measurements were done with a vibration sample magnetometer model 155 at room temperature. The estimation of chlorine was carried out by the usual gravimetric method. Copper was estimated volumetrically$^{(10)}$. Germanium, tin, titanium and zirconium were determined by a reported method$^{(11)}$.

Synthesis of $[Cu(TETA)]Cl_2$

This complex was prepared by dissolving (0.01 mol, 2.42 g) cupric chloride in 30 cm^3 MeOH with dropwise addition of (0.01 mol, 1.46 cm^3) triethylene tetramine. The dark blue product was formed after keeping the mixture overnight and was washed and recrystallized from methanol and dried under vacuum.

Synthesis of $[Cu_2(TETA)_2Cl_4M]$

A hot MeOH solution (50 cm^3) of $[Cu(TETA)]Cl_2$ (0.02 mol, 5.6 g) was treated with (0.01 mol) group IV metal tetrachlorides ($SiCl_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$ and $ZrCl_4$). In each case a yellowish precipitate appeared immediately, which was washed with MeOH and dried under vacuum.

Results and discussion

The analytical data (Table 1) agree well with the compositions $[Cu(TETA)]Cl_2$ and $[Cu_2(TETA)_2Cl_4M]$ (M = Si, Ge, Sn, Ti and Zr; TETA = triethylene tetramine). The reaction of copper(II) chloride with TETA in MeOH yielded $[Cu(TETA)]Cl_2$. Further reaction of this complex with group IV metal tetrachlorides in a 2:1 ratio resulted in the formation of the heterotrinuclear complexes, $[Cu_2(TETA)_2Cl_4M]$. The conductivity measurements in DMSO$^{(12)}$ show that $[Cu(TETA)]Cl_2$ is ionic while the heterotrinuclear chelates are covalent. It has been demonstrated recently$^{(8,9)}$ that such a reaction occurs via the replacement of the aminohydrogen by a group IV metal, and that removal of 4HCl molecules results in a new covalent bond being formed between the nitrogen of the tetramine and the group IV metal. The reactions followed are represented in Scheme 1.

A room temperature e.s.r. spectrum of the $[Cu(TETA)]Cl_2$ gives approximate g-values with $g_{\parallel} = 2.09$ and $g_{\perp} = 2.06$, which favours the square planar geometry around the copper(II) ion$^{(13,14)}$. The apparent g-values of the heterotrinuclear polycrystalline samples are $g_{\parallel} = 1.99$ and $g_{\perp} = 2.07$ with the average g-values $\langle g \rangle = (2g_{\parallel} + g_{\perp}/3 = 2.04)$ being in accord with those of typical octahedral copper(II) complexes$^{(15)}$. On this basis it is suggested that the chloride ions present in $[Cu(TETA)]Cl_2$

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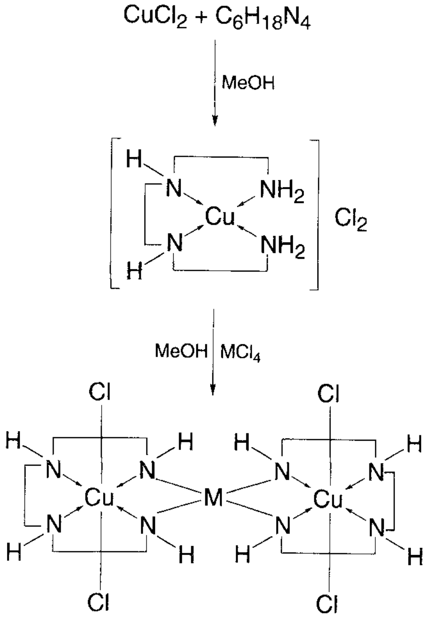
Table 1. Analytical data and colour of the complexes.

Complex	Yield (%)	M.p. (°C)	Colour	Found (Calcd.) (%) C	H	N	Cl	Cu
$C_6H_{18}N_4CuCl_2$	80	200	Blue	25.8 (25.7)	6.5 (6.4)	19.8 (20.0)	25.2 (25.3)	22.4 (22.5)
$C_{12}H_{32}N_8Cu_2Cl_4Si$	60	254	Yellow	24.7 (24.6)	5.5 (5.5)	19.0 (19.2)	24.2 (24.3)	21.1 (21.5)
$C_{12}H_{32}N_8Cu_2Cl_4Ge$	65	261	Yellow	23.1 (22.9)	5.2 (5.1)	17.8 (17.8)	22.0 (22.6)	19.7 (20.0)
$C_{12}H_{32}N_8Cu_2Cl_4Sn$	75	222	Yellow	21.5 (21.3)	4.8 (4.7)	16.0 (16.6)	21.7 (21.0)	18.5 (18.7)
$C_{12}H_{32}N_8Cu_2Cl_4Ti$	60	181	Yellow	23.9 (23.8)	5.2 (5.3)	18.2 (18.6)	23.1 (23.5)	20.5 (20.8)
$C_{12}H_{32}N_8Cu_2Cl_4Zr$	65	156	Yellow	23.0 (22.2)	5.2 (4.9)	17.3 (17.3)	21.9 (21.9)	19.3 (19.4)



Scheme 1. M = Si, Ge, Sn, Ti and Zr

coordinate with copper(II) ion upon complexation with group IV metal tetrachlorides to make up an octahedral environment around the copper(II) ion. As mentioned previously(8,9) chloride ions present in [Cu(TETA)]Cl_2 coordinate to copper(II) ion while the group IV metal chlorines go into solution as HCl. This may be due to (1) the readily available anionic chlorine of [Cu(TETA)]Cl_2 which should, in any case, be a better ligand than the covalently bonded chlorine of group IV metal, (2) since copper(II) achieves an octahedral geometry only after complexation with MCl_4 it is thought that removal of aminohydrogen is done only by the group IV metal chlorine. Otherwise, the chloride ions present in [Cu(TETA)]Cl_2 should have been released in the form of HCl before reaction with MCl_4. This type of compound represents an unprecedented example in a family of $Cu(NN)_2X_2$ chromophores that has retained its octahedral coordination through *trans*-ligation, in spite of the steric effects(16).

The electronic spectrum of [Cu(TETA)]Cl_2 in MeOH shows a high intensity charge transfer band at 247 nm and the ligand–metal charge transfer band at 304 nm. A strong d–d band at 596 nm is also observed which is characteristic of square planar complexes(17). The trinuclear complexes in DMSO also show strong bands at 275 nm, along with shoulders assignable to intra-ligand transition and ligand–metal charge transfer which is in consonance with the observation reported(18,19). The d–d band maxima, at 930 nm and at 882 nm, are due to octahedral bimetallic copper(II) complexes. It is known that octahedral distortion in copper(II) complexes leads to the displacement of d–d bands to lower energies. The observed magnetic moment for all the polycrystalline samples is 1.74 B.M., which is characteristic of one unpaired electron and approximately close to the theoretical value of 1.73 B.M., indicating no magnetic interactions between the two copper(II) ions.

The i.r. spectrum of [Cu(TETA)]Cl_2 exhibits a band at 3270 cm^{-1}, characteristic of the N—H stretching frequency, while a peak at 1584 cm^{-1} is assigned to δ(N—H). In the trinuclear complexes the ν(N—H) appears at a lower wave number (3110 cm^{-1}) suggesting the formation of a group IV metal-nitrogen covalent bond, δ(N—H) remains unaffected. Two sharp absorption bands appear at 1060 cm^{-1} and 1384 cm^{-1} in both the mono- and trinuclear complexes, assigned to ν(C—C) and ν(C—N) modes, respectively. Two further distinct bands appear at 2962 cm^{-1} and 751 cm^{-1}, assigned to ν(C—H) and CH_2 rocking mode, respectively. New bands of medium intensity in 430–525 cm^{-1} range in the complexes have been assigned to ν(M—N). A distinct band appeared in the mono- and the heterotrinuclear complexes at 405 cm^{-1} assigned to the Cu—N stretching frequency. A band appeared in the complexes at 315 cm^{-1} assigned considerably to ν(Cu—Cl), which was absent in the spectra of [Cu(TETA)]Cl_2. The characteristic i.r. bands are given in Table 2. The disappearance of ν(M—Cl) in 220–350 cm^{-1} range in the far i.r. spectra of the trinuclear complexes confirms the replacement of the four chlorines in the group IV metal tetrachlorides.

Table 2. I.r. and far i.r. absorption bands (cm^{-1}) of [Cu(TETA)]Cl_2 and its heterotrinuclear complexes.

Complex	ν(N—H)	ν(Cu—N)	ν(Cu—Cl)	ν(M—N)
$C_6H_{18}N_4CuCl_2$	3270m	405s	–	–
$C_{12}H_{32}N_8Cu_2Cl_4Si$	3110m	403s	315m	430s
$C_{12}H_{32}N_8Cu_2Cl_4Ge$	3112m	403s	315m	485s
$C_{12}H_{32}N_8Cu_2Cl_4Sn$	3112m	403s	315m	455s
$C_{12}H_{32}N_8Cu_2Cl_4Ti$	3110m	403s	315m	420s
$C_{12}H_{32}N_8Cu_2Cl_4Zr$	3110m	403s	315m	425s

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