# A TRANSITION METAL COMPLEX AS A LIGAND IN THE CHEMISTRY OF GROUP (IV) ELEMENTS

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**Abstract**—Heterobimetallic complexes of the type  $[Cu(TETA)Cl_2MCl_2]$  (M = Si, Ge, Sn, Ti and Zr; TETA = triethylene tetramine) have been synthesized and characterized by elemental analyses, ESR, electronic and IR spectra and conductivity measurements. The complex  $[Cu(TETA)Cl_2SnPh_2]$  has also been prepared. The results indicate that  $[Cu(TETA)]Cl_2$  is square planar and ionic in nature, while its bimetallic complexes,  $[Cu(TETA)Cl_2SnPh_2]$ , are covalent with an octahedral environment around the copper(II) ion.

The development of binuclear systems has arisen from the idea that two metal atoms in close proximity could react in a cooperative manner with substrate molecules.<sup>1,2</sup> A major role in the building of binuclear complexes has been played by tertiary diphosphines. bis(diphenylphosphino)methane (dppm) being particularly efficient for this purpose.<sup>3,4</sup> Substitution of one of the donor atoms in the dppm skeleton for a softer (As) or harder (N) centre has been introduced to create heterobinuclear complexes of the platinum group metals. Such ligand systems studied by Balch are (diphenylarsino)(diphenylphosphino)methane (dapm)<sup>5,6</sup> and 2-(diphenylphosphino)pyridine (Ph2PPY), 7-15 which have led to a controlled synthesis of platinumrhodium complexes having two bridging ligands.<sup>16</sup>

The growing interest in electrochemical, magnetic and spectroscopic studies on multimetallic complexes is due to their great importance in biology.<sup>17-24</sup> They are ubiquitous in nature as active sites in a variety of metalloenzymes and are playing a significant role in industrial catalysis. Furthermore, they provide interesting cases for the study of magnetic interaction and may also serve as models in certain cases for some metalloproteins, for which the biological function is associated with the occurrence of metals centres in pairs.

By a judicious choice of the two metals, it is possible to synthesize a large number of multimetallic compounds. Since the heterobimetallic chelates containing group (IV) elements seem to be scarce, it was considered worthwhile to synthesize a number of new heterobimetallic complexes of the type [Cu(TETA)Cl<sub>2</sub>MCl<sub>2</sub>] (M = Si, Ge, Sn, Ti and Zr).

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#### EXPERIMENTAL

Triethylene tetramine (Koch Light), cupric chloride, SiCl<sub>4</sub>, GeCl<sub>4</sub>, SnCl<sub>4</sub>, TiCl<sub>4</sub>, ZrCl<sub>4</sub> (BDH) and Ph<sub>2</sub>SnCl<sub>2</sub> (Fluka) were used as received. Ethanol and DMSO were distilled before use. Microanalyses of the complexes were obtained on a Carlo-Erba Analyser Model 1106. Molar conductance was measured at room temperature on a Digisun electronic conductivity bridge. The IR spectra  $(200-4000 \text{ cm}^{-1})$ were recorded on a Carl-Ziess Specord M-80 spectrophotometer in Nujol mulls. The electronic spectra were recorded on a Shimadzu UV-vis recording spectrophotometer Model 60. The EPR 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. The estimation of chlorine was determined by the usual gravimetric method.

### Synthesis of [Cu(TETA)]Cl<sub>2</sub>

This complex was prepared by dissolving cupric chloride (0.01 mol, 2.42 g) in ethanol  $(30 \text{ cm}^3)$  with dropwise addition of triethylene tetramine  $(0.01 \text{ mol}, 1.46 \text{ cm}^3)$ . The dark blue product was formed after keeping the mixture overnight and was washed, recrystallized from ethanol and dried *in vacuo*.

Synthesis of [Cu(TETA)Cl<sub>2</sub>MCl<sub>2</sub>] and [Cu(TETA) Cl<sub>2</sub>SnPh<sub>2</sub>]

A hot ethanolic solution (15 cm<sup>3</sup>) of [Cu (TETA)]Cl<sub>2</sub> (0.01 mol, 2.8 g) was treated with

group (IV) metal tetrachlorides or diphenyltindichloride (0.01 mol). In each case an immediate precipitate appeared, which was washed with ethanol and dried *in vacuo*. All the synthesized complexes are soluble only in DMSO.

## **RESULTS AND DISCUSSION**

The analytical data (Table 1) conform to the compositions [Cu(TETA)]Cl<sub>2</sub>, [Cu(TETA)Cl<sub>2</sub>MCl<sub>2</sub>] and  $[Cu(TETA)Cl_2SnPh_2]$  (M = Si, Ge, Sn, Ti and Zr; TETA = triethylenetetramine). The reaction of copper(II) chloride with TETA in ethanol yields [Cu(TETA)]Cl<sub>2</sub>. Further reaction of this complex with group(IV) metal tetrachlorides and diphenyltin(IV) dichloride gives high yields of the heterobimetallic chelates [Cu(TETA)Cl<sub>2</sub>MCl<sub>2</sub>] and  $[Cu(TETA)Cl_2SnPh_2]$ , respectively. The conductivity measurements in DMSO<sup>25</sup> show that the ligand [Cu(TETA)]Cl<sub>2</sub> is ionic, while the heterobimetallic chelates are covalent. Therefore, the complexes are formed by the replacement of amine hydrogens by group (IV) metals and the removal of 2HCl molecules, which has also been confirmed by the quantitative estimation of chlorine as AgCl. The reactions followed are represented in Scheme 1.

A room-temperature ESR spectrum of the powdered sample of [Cu(TETA)]Cl<sub>2</sub> 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.<sup>26,27</sup> The apparent g values of the bimetallic 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 accordance with those

Table 1. Analytical data, melting point, colour and % yield of the ligand, [Cu(TETA)]Cl<sub>2</sub>, and its heterobimetallic complexes

	Yield		Melting	Analysis (%) [Found (Calc.)]			
Complex	(%)	Colour	point (°C)	С	Η	N	Cl
[C <sub>6</sub> H <sub>18</sub> N <sub>4</sub> CuCl <sub>2</sub> ]	90	Blue	200	25.7	6.4 (6.4)	20.0	25.3 (25.4)
[C6H16N4CuSiCl4]	80	Yellow	175	19.0 (19.0)	4.2 (4.2)	14.8	37.6
$[C_6H_{16}N_4CuGeCl_4]$	80	Yellow	154	17.0 (17.1)	3.8 (3.7)	13.2 (13.3)	33.6 (33.6)
[C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> CuSnCl <sub>4</sub> ]	80	Yellow	172	15.4 (15.3)	3.4 (3.4)	11.9 (11.9)	30.4 (30.3)
[C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> CuTiCl <sub>4</sub> ]	80	Yellow	155	18.1 (18.1)	4.0 (4.1)	14.1 (14.0)	35.8 (35.7)
[C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> CuZrCl <sub>4</sub> ]	.80	Yellow	160	16.2 (16.3)	3.6 (3.7)	12.6	32.1 (32.1)
$[C_6H_{16}N_4CuSnCl_2(C_6H_5)_2]$	70	Yellow	120	39.2 (39.3)	4.7 (4.7)	10.1 (10.1)	12.9 (12.8)



Where M = Si,Ge,Sn,Ti and Zr

Scheme 1.

of typical octahedral copper(II) complexes.<sup>28</sup> On this basis we suggest that the chloride ions present in [Cu(TETA)]Cl<sub>2</sub> coordinate with copper(II) ions upon complexation with group(IV) metal tetrachlorides to produce an octahedral environment around the copper(II) ion. It is to be noted that the chloride ions present in [Cu(TETA)]Cl<sub>2</sub> coordinate to the copper(II) ion and not the group (IV) metal chlorine. This may be due to (a) the easy availability of the anionic chlorine of [Cu(TETA)]Cl<sub>2</sub>, which should in any case be a better ligand than the covalently bonded chlorine of group (IV) metals and (b) since copper(II) achieves an octahedral geometry only after complexation with MCl<sub>4</sub>, it is thought that the removal of aminohydrogen occurs due to the group (IV) metal chlorine. Otherwise, the chloride ions present in [Cu(TETA)]Cl<sub>2</sub> would have gone as HCl before its reaction with MCl<sub>4</sub>.

The electronic spectra of the mononuclear complex in methanol,  $[Cu(TETA)]Cl_2$ , shows a high intensity charge-transfer band at 247 nm, along with 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.<sup>29</sup> The bimetallic complexes in DMSO also show strong bands at 275 nm, along with the shoulders assignable to intra-ligand transitions and ligand-metal charge-transfer, which is in agreement with the observation reported.<sup>30,31</sup> The d-d band maxima, one at 930 and another 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.<sup>32</sup>

It is possible to assign some of the important IR bands which are helpful in determining the structures of the synthesized complexes. In [Cu (TETA)]Cl<sub>2</sub> the band at 3270 cm<sup>-1</sup> is characteristic of the N—H stretching frequency, while the peak at 1584 cm<sup>-1</sup> is assigned to  $\delta$ (N—H). In the bimetallic

	Peak positions (cm <sup>-1</sup> )								
Complex	v(N-H)	v(Cu—N)	v(CuCl)	v(MN)	v(MCl)				
$[C_6H_{18}N_4CuCl_2]$	3270m	405s							
C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> CuSiCl <sub>4</sub> ]	3110m	403s	315m	430s	300s				
C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> CuGeCl <sub>4</sub> ]	3112m	403s	315m	485s	305s				
C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> CuSnCl <sub>4</sub> ]	3112m	403s	315m	455s	300s				
[C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> CuTiCl <sub>4</sub> ]	3110m	403s	315m	520s	290s				
[C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> CuZrCl <sub>4</sub> ]	3110m	403s	315m	525s	290s				
$[C_6H_{16}N_4CuSnCl_2(C_6H_5)_2]$	3108m	403s	310m	472s	300s				

Table 2. IR and far-IR absorption bands of the ligand, [Cu(TETA)]Cl<sub>2</sub>, and its heterobimetallic complexes

chelates v(N-H) appears at a lower wave number (3110 cm<sup>-1</sup>), suggesting the formation of a group (IV) metal-nitrogen covalent bond, and  $\delta(N-H)$ remains unaffected. Two sharp absorption bands appear at 1060 and 1384 cm<sup>-1</sup> in both the monoand binuclear complexes, assigned to v(C-C) and v(C-N) modes, respectively. Another two distinct bands appear at 2962 and 751 cm<sup>-1</sup>, assigned to v(C-H) and CH<sub>2</sub> rocking modes, respectively.

The far-IR region of the spectra is very significant as it includes the M—N and M—X stretches. The M—X absorption bands are stronger and appear at lower wave numbers compared to M—N absorption bands. New bands of medium intensity in the range 430–525 cm<sup>-1</sup> in the complexes have been assigned to v(M—N). A distinct band appeared in the ligand and the heterobimetallic complexes at 405 cm<sup>-1</sup>, assigned to a Cu—N stretching frequency. A band appeared in the complexes at 315 cm<sup>-1</sup>, assigned to v(Cu—Cl), which was absent in the spectra of the free ligand, [Cu(TETA)]Cl<sub>2</sub>. Sharp bands appeared in the complexes in the range 290–305 cm<sup>-1</sup> and are attributed to v(M—Cl). The characteristic IR bands are given in Table 2.

In further communications our interest lies in reporting the results of the reaction between  $[Cu(TETA)](BF_4)_2$  and  $[Cu(TETA)]Br_2$  with group (IV) metal tetrachlorides and organotin(IV) chlorides.

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