

Synthesis of Triphenylmethylphosphonium Salts of Transition Metal Halides

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Summary

Triphenylmethylphosphonium salts namely $[\text{PPh}_3 \text{ Me}]_a \text{MX}_n$, $\text{M} = \text{Cu}^{2+}$, Co^{2+} , Mn^{2+} , Fe^{3+} , Pb^{2+} and Hg^{2+} , $\text{X} = \text{Cl}$ or I , $a = 1$ or 2 , have been synthesized by the reaction of $\text{PPh}_3 \text{ Me X}$ with the metal dihalide in ethanol solutions. The compounds were characterized by Electronic, Raman, Far infrared and Mossbaur spectra, magnetic properties as well as elemental analyses. The two copper complexes $(\text{PPh}_3 \text{ Me})_2 \text{CuCl}_4$ and $(\text{PPh}_3 \text{ Me})_2 \text{Cu}_3\text{Cl}_8$ have been characterized by their X-ray crystallography and the structures are described. Powder diffraction patterns have shown that the cobalt and manganese tetrachloride complexes are isomorphous. Investigation of the complexes by differential scanning calorimetry measurements showed that these compounds exhibited structural phase transitions.

Introduction

In compounds of the form $\text{A}_2 \text{MX}_4$ (where $\text{A} =$ monovalent cation, $\text{M} =$ divalent transition or nontransition metal ion and $\text{X} =$ halogen), the nature of the cation influences greatly the structure of the MX_4^{2-} moiety. If M^{2+} ions were each octahedrally surrounded by halogen ions, the octahedra would share corners and extend in an infinite two dimensional network, whereby the layers become held together by the cation. The MX_4^{2-} moiety on the other

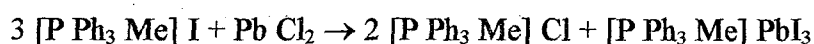
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have been of particular interest in such compounds. Extensive studies of compounds containing alkyl ammonium groups, showed that the hydrogen bonds and thermal motion of the alkyl ammonium groups can induce structural phase transitions⁽¹⁻⁴⁾. As a further extension of the above studies, the synthesis of analogous salts in which the central nitrogen atom of the cation was replaced by higher members of the pnictogen group: P, As and Sb⁽⁵⁻⁸⁾ was reported. The latter compounds have received much current interest. Here I wish to report the results of the study of the synthesis, structure and phase transitions of a novel family of [PPh₃Me]⁺MX_n⁻ salts.

Experimental

All chemicals used are of AR grade. The electronic spectra of saturated solutions of the separated chloride complexes dissolved in methylene chloride were recorded using Superscan 3 UV / Vis Spectrophotometer. Raman spectra of all samples were recorded with a laser $\lambda = 514,5$ nm using Spectrophotometer, model 2061 supplied by Jobin Yvon Division Instruments. Far - Infrared spectra ($300-50$ cm⁻¹) were obtained for solid pellets of samples of compressed polyethylene and were recorded with Nicolet 2F Vacuum Spectrophotometer. Differential scanning calorimetry measurements were recorded with shimadzu DSC-50 Instrument.

[P Ph₃ Me]⁺ Cl⁻ was prepared as follows:



Pb Cl₂ (2.781g, 10 mm) was dissolved in hot water so as to form a concentrated solution. An aqueous solution of [PPh₃Me]⁺ I⁻ (12.127 g, 30 mm) was added dropwise with stirring, whereby the yellow precipitate of

[PPh₃Me] PbI₃ formed was filtered off. The solvent in the filtrate was evaporated using a rotatory evaporator. The solid residue left was dissolved in ethyl alcohol and the solution was filtered to get rid of any residue of PbCl₂. The filtrate was again evaporated to dryness under vacuum.

Preparation of Triphenylmethylphosphonium Salts

The compounds were prepared by adding together ethanolic solutions of the respective metal chloride and [PPh₃Me] Cl, in molar ratios of 1:2, respectively, then evaporating the products nearly to dryness. In case of the copper complex the addition of 1:2 ratios led to the formation of both yellow and red crystals. On the other hand the addition of 1: 2.5 molar ratios would lead to the formation of the yellow [PPh₃Me]₂ CuCl₄ complex, whereas the addition of 1 : 1 molar ratios led to the formation of the red [PPh₃Me]₂ Cu₃ Cl₈ compound. The [PPh₃Me] Fe Cl₄ complex was also prepared by mixing equimolar amounts of [PPh₃Me] Cl and ferrous chloride in HCl acidified ethanol solution. Slow evaporation at room temperature resulted in pale yellow plate-like crystals. The compounds prepared were washed with a mixture of ether and ethanol and dried in a dessicator. The salts dissolved in ethanol and methylene chloride and crystallize readily form concentrated solutions. The physical constants of the complexes prepared are given in Table1.

It should be pointed out that trials to synthesize stable transition metal iodide salts of the formula [PPh₃Me]_a M I_n was unsuccessful. The metal iodides decomposed and catalyzed the formation of the phosphonium polyio-

dide $[\text{PPh}_3\text{Me}] \text{I}_3$ ⁽⁹⁾. However it was possible to synthesize salts of some main group metal iodides for example $[\text{PPh}_3\text{Me}] \text{Pb I}_3$ and $[\text{PPh}_3\text{Me}]_a \text{HgI}_n$. (Table 1)

Results and Discussion

It is reported that divalent chlorocuprates may contain isolated CuCl_4^{2-} moieties, di or oligomer aggregates. In the work represented here two copper complexes were synthesized the yellow $[\text{PPh}_3\text{Me}]_2 \text{Cu Cl}_4$ (1) and the red $[\text{PPh}_3 \text{Me}]_2 \text{Cu}_3\text{Cl}_8$ (2). The electronic absorption spectrum of compound (1) gave a broad band with λ_{max} at 880 nm which indicates that the complex exhibited a distorted tetrahedral structure. The vibrational spectra showed an ir band at 283 cm^{-1} and a Raman shift at 279.5 cm^{-1} assignable to Cu-Cl stretching vibrations. Such bands also reflect the distorted tetrahedral structure. Complete X- ray crystal structure analysis⁽¹⁰⁾ reveals that complex (1) at 293 °K is orthorhombic with space group F2dd where $a = 8.840(5) \text{ \AA}$, $b = 25.152 (5) \text{ \AA}$ $c = 32.791 (8) \text{ \AA}$, $V = 7291 (5) \text{ \AA}^3$, $Z = 8$. The crystal structure has been refined to $R = 0.038$ for 1765 reflections. It contains the cations $[\text{PPh}_3\text{Me}]^+$ and the isolated complex anions $[\text{CuCl}_4]^{2-}$. The cations are composed of planer against each other twisted phenyl groups tetrahedrally arranged around the central phosphorous atoms. The complex anion CuCl_4^{2-} has a flattered tetrahedral geometry possessing a two fold rotation axis. This is in accordance with many reported complexes⁽¹¹⁻¹⁴⁾. The stereo view of the atoms in the complexes are given in Fig 1a. The crystal structure is shown in Fig.2a.

The crystal structure investigation of complex (2) show that it crystallizes at 239°K in triclinic space group with $a = 9.539 (8) \text{ \AA}$, $b = 10.369 (3) \text{ \AA}$, $c = 11.059 (5) \text{ \AA}$, $\alpha = 87.70 (3)^\circ$, $\beta = 67.25 (2)^\circ$, $\gamma = 84.28 (4)^\circ$, $V = 1004 (1) \text{ \AA}^3$, and $Z = 1$. The crystal structure has been refined to $R = 0.032$ for 4436 reflections It is polynuclear containing the tetrahedral cations $[\text{PPh}_3\text{Me}]^+$ previously described, and the chain anion $[\text{Cu}_3\text{Cl}_8]^{2-}$ with four and fivefold coordinated divalent copper atoms. (Fig. 1b). The anion is composed of Cu1 with nearly square planar surrounding of chloride ions possessing an inversion center, and Cu2 with square pyramidal geometry. Two square pyramids share the edges of the square planer unit forming an inversion center. The electronic spectrum of compound (2) shows two bands at 474 and 887 nm. Compound (2) exhibits numerous ir bands principally occurring at 356,88, 319.95, 287.43 and 243 cm^{-1} which might be due to Cu-Cl stretching vibrations in contrast to compound (1) which shows only one ir vibrational band and one raman shift due to the Cu-Cl stretching vibration. The structure possesses terminal and bridged Cu-Cl bonds, which explains the numerous vibrational bands observed in the ir spectrum. Polynuclear cholrocuprate anions do not occur frequently. Dimeric moieties $\text{Cu}_2\text{Cl}_6^{2-}$ are found in $[\text{Ph}_4\text{P}]_2\text{CuCl}_6^{(15-16)}$. Trinuclear units $\text{Cu}_3\text{Cl}_8^{2-}$ exist in $(3\text{MAP})_2\text{Cu}_3\text{Cl}_8$ and in $(\text{NMPZ})_2\text{Cu}_3\text{Cl}_8^{(17)}$. Trinuclear anions could unit together forming chains as in $(\text{H}_2 \text{ aza})_3[\text{Cu}_3\text{Cl}_8(\text{H}_2\text{O})_3]^{(18)}$ and $[\text{adeH}_2][\text{Cu}_3\text{Cl}_8]^{(19)}$ in which the coordination sphere is completed by O or N. Polynuclear chain anions $[\text{Cu}_3\text{Cl}_8]^{2-}$ are also found in $\{[\text{Me}(\text{CN})_2 \text{ Mg } 15\text{C}5][\text{Cu}_3 \text{ Cl}_8]\}_n^{(20)}$ and $\{[\text{Me}(\text{CN})_2 \text{ Cu}15\text{C}5][\text{Cu}_3 \text{ Cl}_8]\}_n^{(21)}$ which only comprise bridging chlorides in contrast to

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complex (2) shown in Fig. 1b which has bridging and terminal chlorides. The crystal structure is shown in fig2b.

The blue cobalt compound $[\text{PPh}_3\text{Me}]_2\text{CoCl}_4$ gave a magnetic moment value of 4.34 B.M. as well as the absorption band at 658.5 nm, which was relatively displaced to lower energy in contrast to octahedrally ligated Co^{2+} . It could be assumed that Co^{2+} has been tetrahedrally surrounded by four chloride ions. The ir bands due to Co-Cl stretching vibrations occurring at 301.3 cm^{-1} with a shoulder at 310 cm^{-1} together with a very strong broad band at 281.64 cm^{-1} (which over-laps with that due to C-P deformation) and the Raman shift observed at 260 cm^{-1} , also confirm the tetrahedral structure.

The isolated manganese triphenylmethylphosphonium complex $[\text{PPh}_3\text{Me}]_2\text{MnCl}_4$ was found to have a magnetic moment of 5.6 B.M in accordance with a compound of high spin magnetic moment. The infrared absorption bands occurring at 287.51 cm^{-1} with a shoulder at 300 cm^{-1} and the relatively strong broad band at 270.07 cm^{-1} , due to the Mn-Cl stretching vibrations shown by the canary yellowish green compound may be taken as indicative that Mn is tetrahedral coordinated. Its electronic absorption spectrum showed bands at 430, 444.1, 632, 668, 699.3 and 828.1 nm. The x-ray powder patterns of Co and Mn compounds would reveal isostructure (Fig. 3). It may however be described that the copper complex (1) have different diffraction pattern, (Fig 3 -b). The determination of the structure of these materials are in progress.

Elemental analysis and ir spectrum (band 3200 cm^{-1}) indicated that the nickel complex $[\text{PPh}_3\text{ Me}]_2\text{ Ni Cl}_4 \cdot 2\text{H}_2\text{O}$ contained two molecules of water which are coordinated to Ni yielding an octahedral structure. The 6- covalent octahedral paramagnetic complexes of Ni showed magnetic moment of values lying between 2.9 - 3.3 B.M. The nickel compound investigated exhibits a moment of 2.8 B.M. at room temperature confirming the octahedral structure. The visible absorption spectrum gave two bands at 650 and 700 nm, which supports the octahedral structure. This compound is essentially similar to $\text{Ni Cl}_4 \cdot (\text{H}_2\text{O})_2 \cdot \text{Rb}_2$ ⁽²²⁾. The bands corresponding to Ni- Cl vibrations, which appear at 246, 240, 200 cm^{-1} confirmed the distorted octahedral structure in which the H_2O ligands are in equatorial position.

The triphenylmethyl Fe (III) complex $[\text{PPh}_3\text{ Me Fe Cl}_4]$ crystallizes in a layered type structure whereby the metal ion is surrounded by a highly symmetric octahedron of chloride ions. These octahedra share corners and extend in an infinite two dimensional network. These layers are sandwiched between the $[\text{PPh}_3\text{ Me}]^+$ cations. No quadrupole splitting is shown in the Mossbauer spectrum of the iron compound (Fig 4). Only one isomer shift in the positive direction (at 0.1 mm / sec) was observed. This proved, that it is a spin free Fe (III) in highly symmetric octahedral surroundings ⁽²³⁾. Its Raman and Far infrared spectra, also confirm the octahedral structure of $\text{Fe}^{(24)}$. The ν_1 (A 1 g), ν_2 (E g) and ν_5 (F 2 g) centrosymmetric vibrational frequencies characteristic for octahedral symmetry are Raman active and appear at 337.5 (v s) , 391 (m) and 85 (w) cm^{-1} whereas, the asymmetric frequencies ν_3 (F 1 u) and ν_4 (F 1 u) are active in the ir spectrum and were

observed at 136.96 (v s) and 83 (w) cm^{-1} , respectively. Also lattice modes at 68 cm^{-1} occur in the Raman and ir spectra.

Phase Transitions in the Triphenylmethylphosphonium Salts

DSC measurements of the yellow copper compound (1) showed exothermic structural phase transitions (Fig. 5). The first occurred at 52.92°C of 72 mJ (4.50 J/g) and the second at 125.62°C of 17.47 mJ (10.92 J/g). The x-ray diffraction patterns taken at -13°C showed that there is no phase transformation. The variation shown in the relative intensities of the diffraction lines may be attributed to some preferred orientation in the investigated sample.

The Mn complex showed three exothermic structural phase transitions. The first occurred at 53.08 °C of 6.01 mJ (3.54 J/g), where as the second transition at 88.76 °C of 2.65 mJ (1.56 J/g) and the third at 125.76 °C of 17.78 mJ (10.46 J/g). The x-ray diffraction pattern taken at 142° C has the same symmetry as that at room temperature. The unit cell with cubic symmetry and lattice parameter $a = 15,5616 \text{ \AA}$ at room temperature and 15,6322 Å at 142 °C, only expanded with the rise of temperature (Fig. 6).

In quaternary ammonium metal salts; it has been indicated⁽¹⁻⁴⁾ that phase transitions were due to the reorientation of the aliphatic groups about their axis between two or more equivalent positions (exchange of the hydrogen bonds between bridging and non bridging chloride ions). On the other hand, the phase transitions in the different phosphonium complexes reported here seem to occur as a results of the thermal displacements involving rotation and translation of the tetrahedra^(7,25).

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Table 1. The physical constant of the complexes prepared

Compound	Colour	m.p °C	Analysis Found (cal.) %		
			C	H	M
$[\text{P Ph}_3 \text{ Me}]_2 \text{ Cu Cl}_4$	yellow	decomp. at 167	59.5 (59.99)	5.1 (4.77)	8.9 (8.36)
$[\text{P Ph}_3 \text{ Me}]_2 \text{ Cu}_3 \text{ Cl}_8$	red	180	45.1 (44.31)	3.9 (3.5)	18.4 (18.5)
$[\text{P Ph}_3 \text{ Me}]_2 \text{ Co Cl}_4$	blue	decomp. at 165	59.1 (60.36)	5.0 (4.80)	7.95 (7.80)
$[\text{P Ph}_3 \text{ Me}]_2 \text{ Mn Cl}_4$	yellowish green	decomp. at 190	60.8 (60.68)	5.1 (4.83)	7.07 (7.31)
$[\text{P Ph}_3 \text{ Me}]_2 \text{ Ni Cl}_4 \cdot 2\text{H}_2\text{O}$	light green	decomp. at 150	57.2 (57.63)	5.1 (5.09)	7.62 (7.42)
$[\text{P Ph}_3 \text{ Me}] \text{ Fe Cl}_4$	pale yellow	172	48.4 (48.05)	4.0 (3.82)	11.8 (11.75)
$[\text{P Ph}_3 \text{ Me}] \text{ Pb I}_3$	canary yellow	230	26.5 (26.38)	2.3 (2.10)	24.1 (23.95)
$[\text{P Ph}_3 \text{ Me}] \text{ Hg I}_3$	canary yellow	173	39.2 (39.06)	3.2 (3.11)	34.4 (34.33)
$[\text{P Ph}_3 \text{ Me}]_2 \text{ Hg I}_4$	white	147	51.1 (50.88)	4.1 (4.05)	21.9 (22.36)

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"تخليق املاح ثلاثى فنيل ميثيل فسفور العناصر الانتقالية"

مرفت مصطفى العيسوى

قسم الكيمياء - كلية العلوم - جامعة القاهرة - مصر

ملخص البحث

تم تخليق هاليدات ثلاثى فنيل ميثيل فسفور عناصر النحاس، الكوبلت، المنجنيز، الحديد ، الرصاص والزنك.

درست خواص المتراكبات وتركيبها بواسطة أطياف الأشعة تحت الحمراء الرامن موس باور، والسينية وأيضا الخواص المغناطيسية.

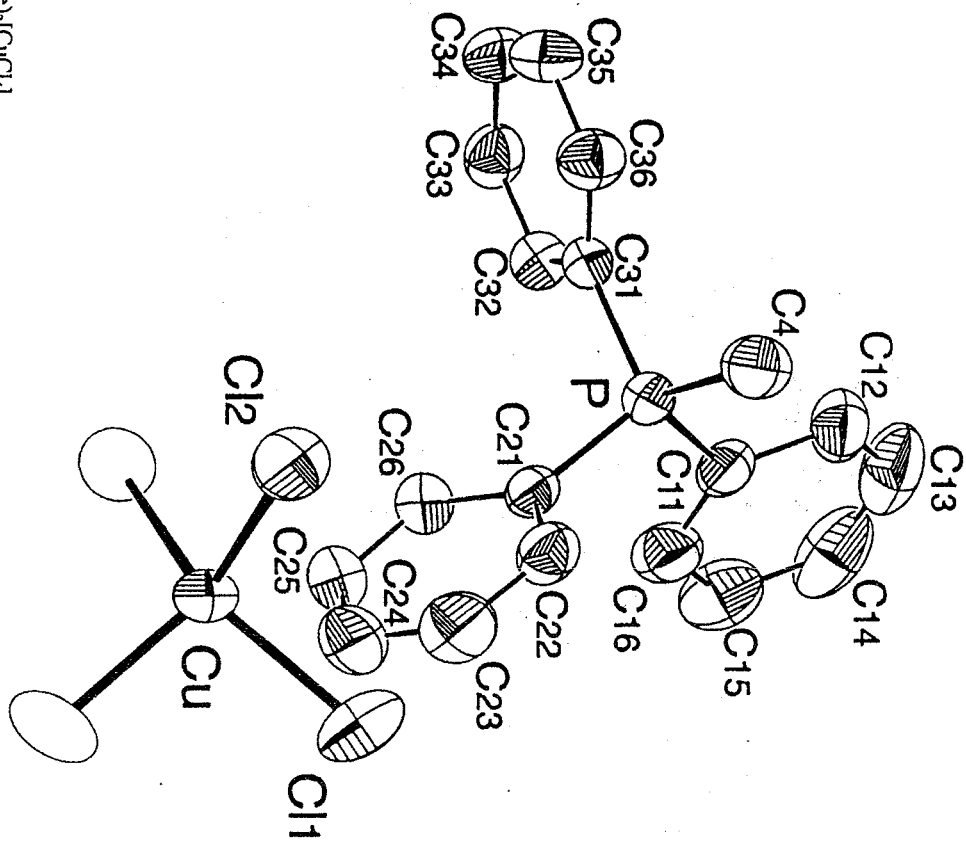


Fig. 1a: $(PPh_3Me)_2[CuCl_4]$

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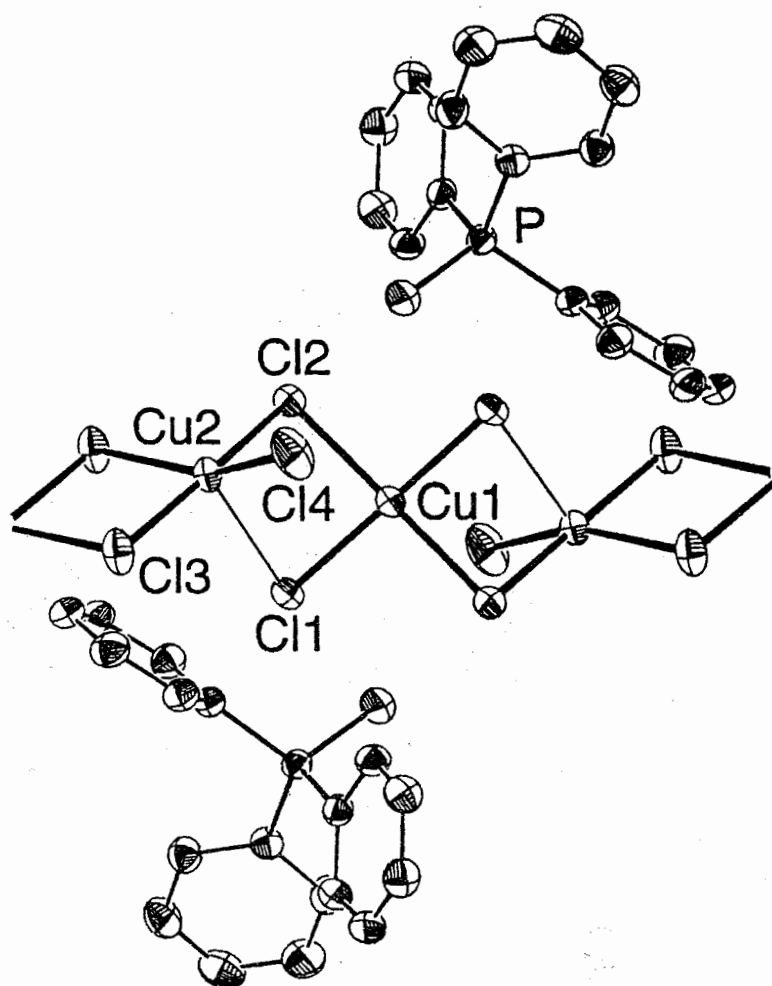
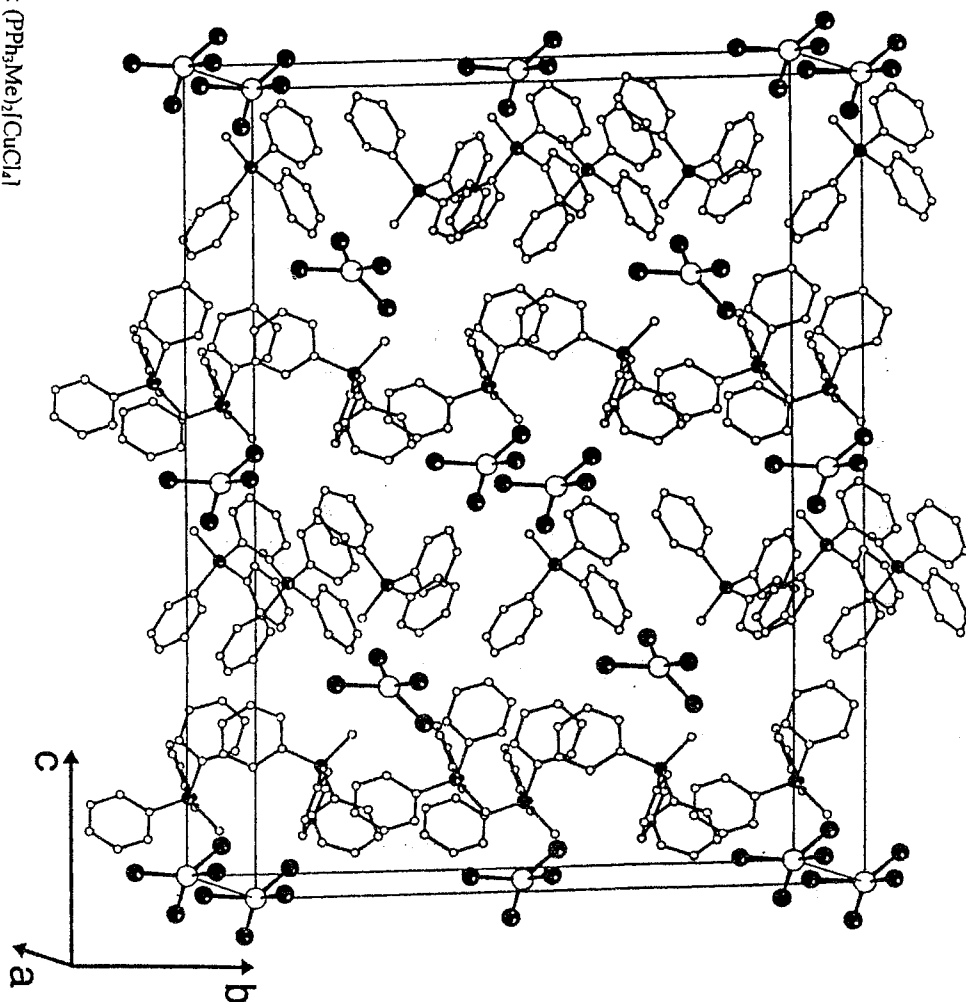


Fig. 1b: $(\text{PPh}_3\text{Me})_2[\text{Cu}_3\text{Cl}_8]$

Fig. 2a: $(\text{PPh}_3\text{Me})_2[\text{CuCl}_2]$



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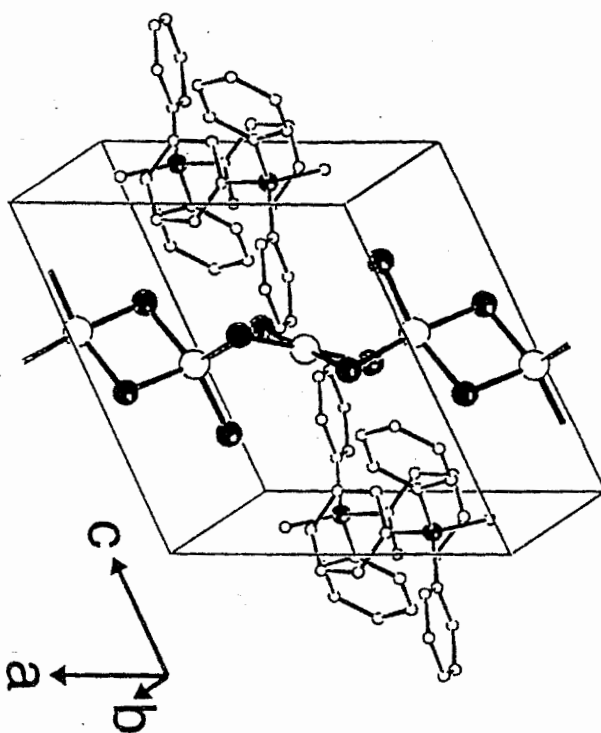


Fig. 2b: $(\text{PPh}_3\text{Me})_2[\text{Cu}_2\text{Cl}_4]$

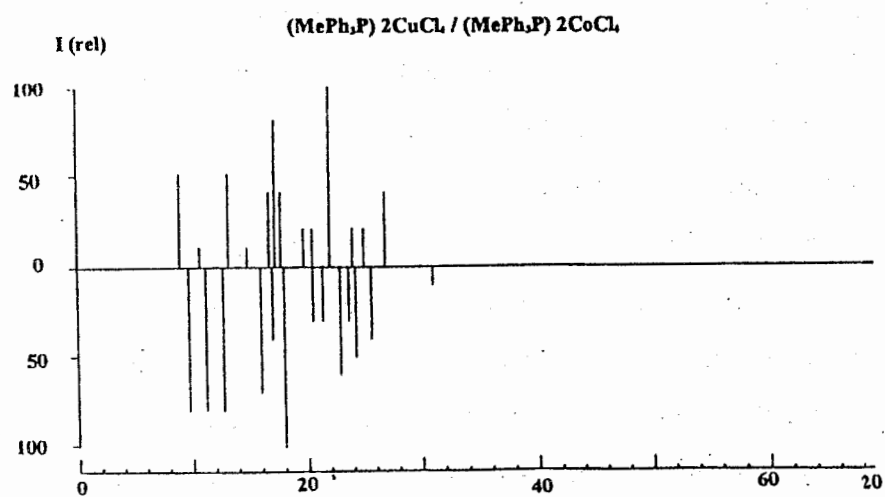
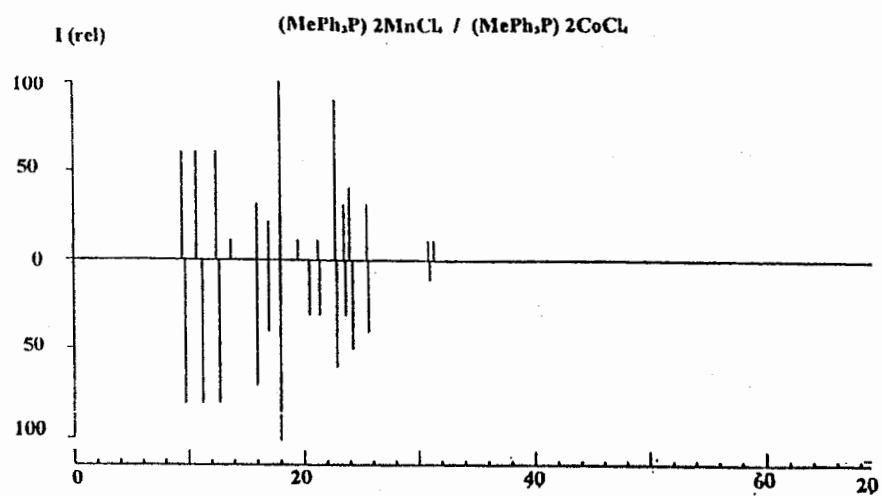


Figure 3 (a - b) X-Ray Powder Diffraction Patterns

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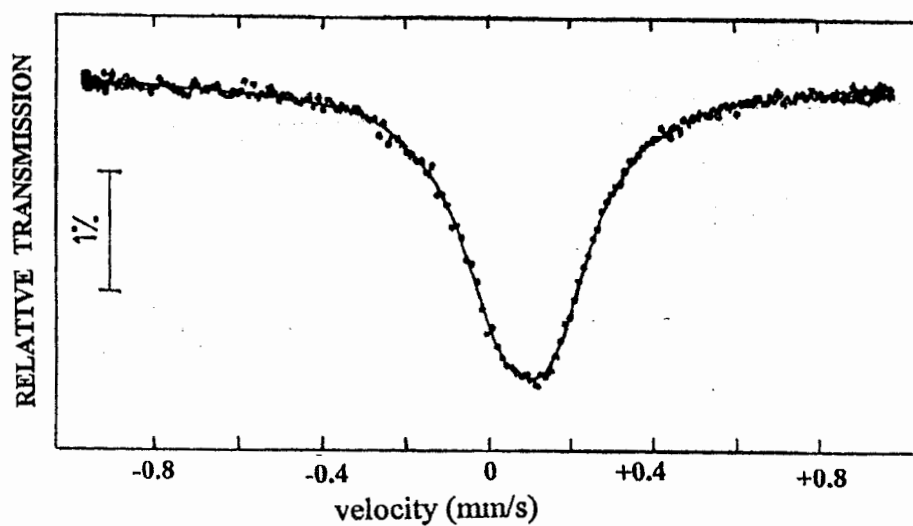


Figure (4) Mössbauer Spectrum of the Fe(III) complex [P Ph₃ Me] Fe Cl₄

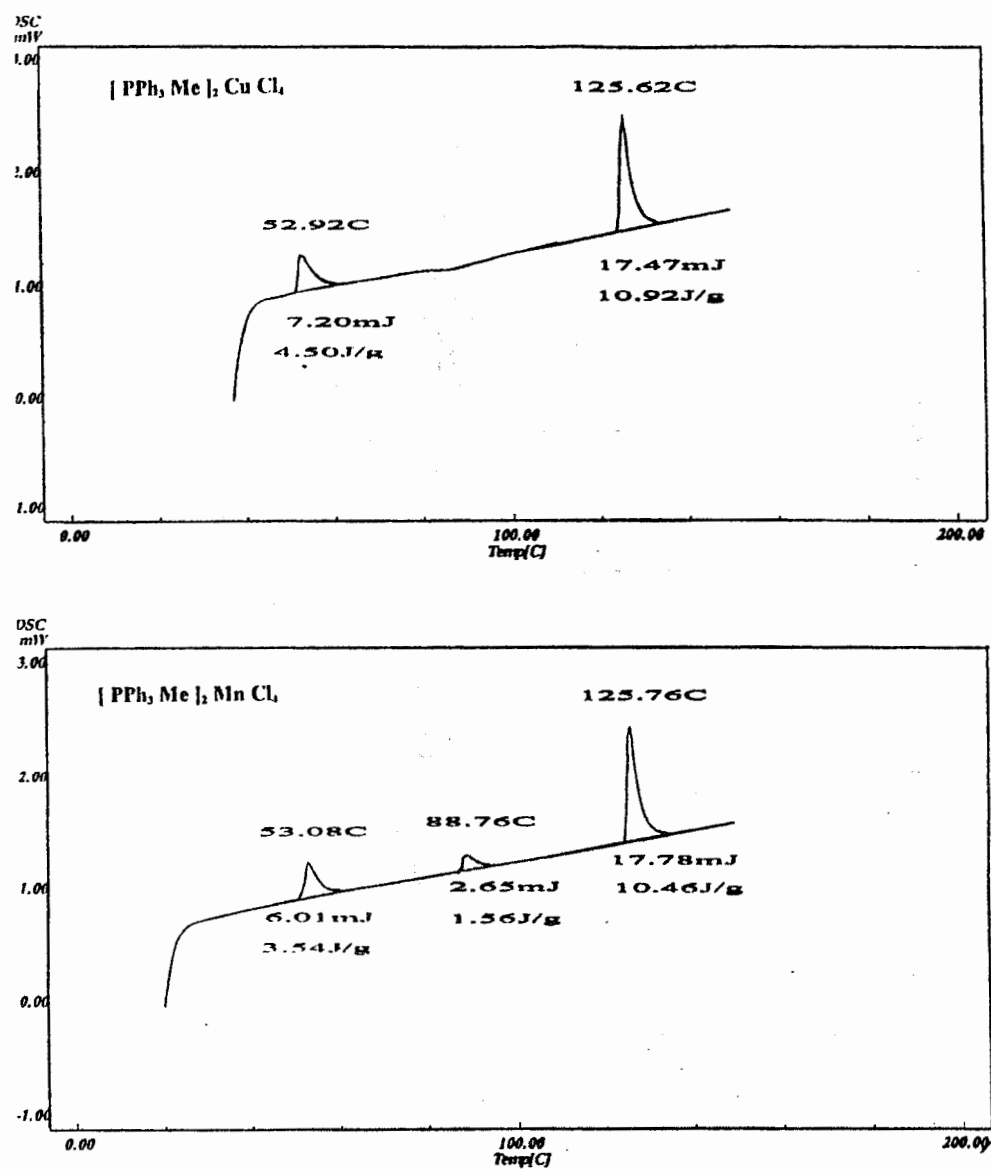


Figure (5) DSC Measurements

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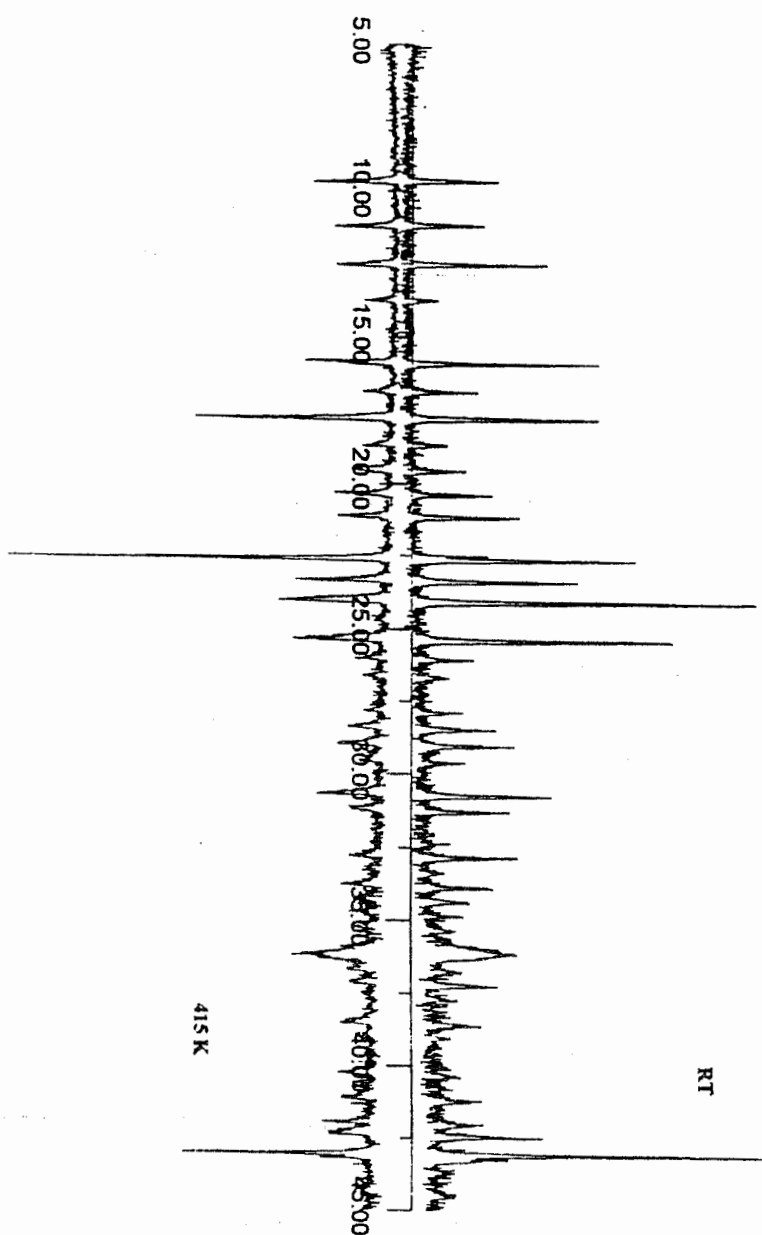


Figure (6) X-ray powder diffraction pattern of (PPh₃)₃Me₂MnCl₄ taken at room temperature and 415 K.