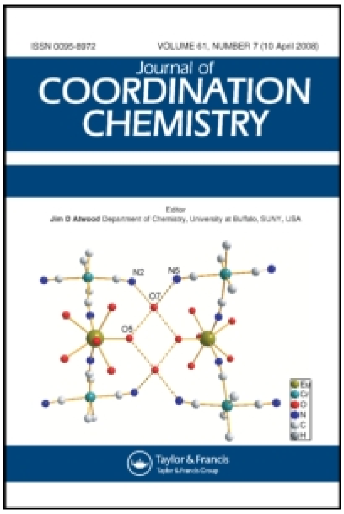

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Structural and vibrational properties of dichlorobis (triphenylphosphineoxide) copper(ii)

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STRUCTURAL AND VIBRATIONAL PROPERTIES OF DICHLORO*BIS* (TRIPHENYLPHOSPHINEOXIDE) COPPER(II)

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Dichloro*bis*(triphenylphosphineoxide)copper(II) has been prepared as a side product and a subunit of tetranuclear μ_4-oxo bridged complexes. The molecular structure, already known in the literature, was redetermined using X-ray diffraction and slight diffrences are discussed. The far IR spectra were recorded and assigned. Structural features of the distorted tetrahedral coordination sphere of copper(II) have been elucidated by performing a vibrational analysis based on quantumchemical calculations using DFT methods.

Keywords: dichlorobis(triphenylphosphineoxide)copper(II); crystal structure; FTIR spectroscopy; quantumchemical calculations

INTRODUCTION

Studying μ_4-oxo bridged tetranuclar Cu(II) complexes[1–4] we obtained the title compound when attempting to obtain single crystals by recrystallisation. This substance represents in a way a subunit of the tetranuclar species. As some of the features of its already published crystall structure[5] did not completely confirm our expectations based on experience with the tetranuclar species we felt encouraged to reinvestigate the crystal structure and to perform experiments on its far IR vibrational properties. Obviously there was some interest to

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elucidate the spectroscopic features of the copper coodination centre in the far IR region. Therefore, the substrate was prepared according to the literature[5] and recrystallized to obtain single crystals for structural investigations. Spectroscopic measurements in the far and mid IR regions have been paralleled by quantumchemical calculations.

EXPERIMENTAL AND THEORETICAL METHODS

Collection and Reduction of the X-Ray Data

Needle-like yellow crystals (melting point 174–175 °C) have been investigated by means of single-crystal X-ray diffraction methods to yield the unit cell and reveal the complete molecular structure. Some slight discrepancies with the published structure of Bertrand[6] have been corrected. Intensities were measured using a Philips PW1100 four-circle diffractometer using graphite monchromatized MoKα radiation. A yellow crystal fragment of size 0.24 × 0.24 × 0.40 mm was investigated. Cell dimensions (see Table I) were determined from +/– Θ scans of 25 reflections with $\Theta = 2$ –20 °. The intensities of 3115 reflections with $\Theta < 25°$, $0 \leq h \leq 37$, $0 \leq k \leq 24$, $0 \leq l \leq 11$, were measured by ω scans with scan widths of 0.8° + 0.32°tanΘ and a scan speed of 2° min^{-1}. Three standard reflections were monitored every two hours and showed insignificant fluctuations (max. +/– 0.8%). The data were corrected for *LP* and absorption effects (μ = 0.955 mm^{-1}). Merging yielded 1540 independent non-extinct reflections (R_{int} = 0.028) of which 1390 had $F \geq 4\sigma(F)$.

TABLE I Crystallographic and experimental data for $CuCl_2[(C_6H_5)_3PO]_2$

Empirical formula	$C_{36}H_{30}Cl_2O_2P_2Cu$
Formula weight	690.98
Temperature	294(1) K
Wavelength	0.71069 Å
Crystal system	Orthorhombic
Space group	*Fdd*2 (No.43)
Unit cell dimensions	a = 31.938(2) Å
	b = 9.890(1) Å
	c = 20.837(1) Å
Volume	6581.7(8) Å^3
Z	8
Density (calculated)	1.395 Mg m^{-3}
Absorption coefficient	0.955 mm^{-1}
F(000)	2840
Theta range for data collection	2.98° to 25.02°
Reflections collected	3115
Independent reflections	1540 [R(int) = 0.0275]
Absorption correction	Gaussian integration (program SHELX76)

TABLE I *(Continued)*.

Transmission factors	0.7655 – 0.8592
Structure solution	Direct methods (program MULTAN78)
Refinement method	Full-matrix least-squares on F^2 with program SHELXL93
Absolute structure parameter	0.09(2)

The structure was solved by direct methods using the program *MULTAN*78.[7] Structure refinement on F^2 was carried out with the program *SHELXL*93.[8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference map and were inserted in idealized positions and refined with a riding model using the program *SHELXL*93 defaults (tertiary C-H 0.98 Å). The isotropic temperature factors of the H atoms were restricted to be proportional to the U_{eq} of their carrier atoms (1.2* U_{eq}). An isotropic correction for extinction was applied. The final full-matrix least-squares refinement varied 196 parameters and used all 1450 independent reflections weighted by $w = 1/[\sigma^2(F_0^2) + (0.039P)^2 + 7.98P]$ where $P = (F_0^2{+}2\ F_c^2)/3$. Final $R = \Sigma||F_0| - |F_0||/\Sigma|F_0|$, $R_w = [\Sigma(w(F_0^2 - F_c^2)^2)/\ \sigma\ (W\ (F_0^2]^{1/2} = 0.076$ and $S = 1.07$ for all data; $R = 0.030$ for the 1390 reflections with $F_0 \geq 4\sigma(F_0)$. The final difference Fourier map showed minimum and maximum values of −0.39 and 0.47 e Å^{-3}. A summary of crystallographic and experimental data is given in Table I. Table II and Table III give non-hydrogen positions and bond lengths and angles. H atom positions, anisotropic thermal parameters, least-squares planes data and structure factors are available from the authors. Chemical analysis agreed with the proposed structure.

TABLE II Atomic coordinates and equivalent isotropic displacement parameters [Å^2] for $CuCl_2[(C_6H_5)_3PO]_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cu	0.25	0.25	0.2500(1)	0.037(1)
Cl	0.2339(1)	0.3269(1)	0.1178(2)	0.111(1)
P	0.3192(1)	0.3370(1)	0.4306(1)	0.036(1)
O	0.2857(1)	0.2905(2)	0.3941(3)	0.048(1)
C(11)	0.3655(1)	0.3282(2)	0.3291(5)	0.040(1)
C(12)	0.3731(2)	0.2701(2)	0.2643(6)	0.052(1)
C(13)	0.4079(2)	0.2632(3)	0.1829(6)	0.064(2)
C(14)	0.4351(2)	0.3132(3)	0.1639(6)	0.062(2)
C(15)	0.4280(2)	0.3709(3)	0.2285(6)	0.062(2)
C(16)	0.3935(2)	0.3783(2)	0.3105(6)	0.053(1)
C(21)	0.3038(1)	0.4199(2)	0.4131(5)	0.037(1)
C(22)	0.3020(1)	0.4473(2)	0.2854(5)	0.045(1)
C(23)	0.2899(2)	0.5109(2)	0.2710(6)	0.053(1)
C(24)	0.2795(2)	0.5464(2)	0.3816(6)	0.058(1)
C(25)	0.2804(2)	0.5194(2)	0.5088(7)	0.060(1)
C(26)	0.2929(2)	0.4559(2)	0.5257(5)	0.048(1)
C(31)	0.3318(1)	0.3255(2)	0.6066(5)	0.042(1)

TABLE II *(Continued).*

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C(32)	0.3663(2)	0.3527(3)	0.6678(6)	0.067(2)
C(33)	0.3729(2)	0.3446(4)	0.8046(7)	0.088(2)
C(34)	0.3457(3)	0.3115(4)	0.8808(8)	0.099(3)
C(35)	0.3123(3)	0.2823(5)	0.8221(8)	0.111(3)
C(36)	0.3055(2)	0.2885(4)	0.6834(7)	0.079(2)

TABLE III Bond lengths [Å] and angles [°] for $CuCl_2[(C_6H_5)_3PO]_2$

Cu-O	2.011(3)	O-P-C(11)	112.9(2)
Cu-O#1	2.011(3)	O-P-C(21)	113.9(2)
Cu-Cl	2.132(2)	O-P-C(31)	108.0(2)
Cu-Cl#1	2.132(2)	C(11)-P-C(21)	105.6(2)
P-O	1.488(3)	C(11)-P-C(31)	110.0(2)
P-C(11)	1.796(5)	C(31)-P-C(21)	106.3(2)
P-C(31)	1.802(5)		
P-C(21)	1.804(4)	P-O-Cu	148.5(2)
C(11)-C(16)	1.388(6)		
C(11)-C(12)	1.391(6)	C(16)-C(11)-P	121.9(4)
C(12)-C(13)	1.380(8)	C(12)-C(11)-P	119.4(4)
C(13)-C(14)	1.371(8)	C(16)-C(11)-C(12)	118.7(4)
C(14)-C(15)	1.381(8)	C(13)-C(12)-C(11)	120.1(5)
C(15)-C(16)	1.377(7)	C(14)-C(13)-C(12)	120.8(5)
C(21)-C(26)	1.387(7)	C(13)-C(14)-C(15)	119.6(5)
C(21)-C(22)	1.387(7)	C(16)-C(15)-C(14)	120.1(5)
C(22)-C(23)	1.388(7)	C(15)-C(16)-C(11)	120.7(5)
C(23)-C(24)	1.362(8)	C(26)-C(21)-P	120.6(4)
C(24)-C(25)	1.379(8)	C(22)-C(21)-P	119.5(3)
C(25)-C(26)	1.391(7)	C(26)-C(21)-C(22)	119.9(4)
C(31)-C(36)	1.371(8)	C(21)-C(22)-C(23)	119.9(5)
C(31)-C(32)	1.379(7)	C(24)-C(23)-C(22)	120.3(5)
C(32)-C(33)	1.380(9)	C(23)-C(24)-C(25)	120.4(5)
C(33)-C(34)	1.340(11)	C(24)-C(25)-C(26)	120.3(5)
C(34)-C(35)	1.358(11)	C(21)-C(26)-C(25)	119.3(5)
C(35)-C(36)	1.395(10)	C(36)-C(31)-P	118.2(4)
		C(32)-C(31)-P	123.2(4)
O-Cu-O#1	89.72(2)	C(36)-C(31)-C(32)	118.5(5)
O-Cu-Cl#1	127.81(1)	C(31)-C(32)-C(33)	120.1(7)
O#1-Cu-Cl	127.81(1)	C(34)-C(33)-C(32)	121.1(7)
O#1-Cu-Cl#1	104.88(1)	C(33)-C(34)-C(35)	119.9(7)
O-Cu-Cl	104.88(1)	C(34)-C(35)-C(36)	120.1(8)
Cl#1-Cu-Cl	104.31(1)	C(31)-C(36)-C(35)	120.2(7)

Symmetry transformations used to generate atoms #1 $-x + 1/2$, $-y + 1/2$, z.

Spectroscopic Investigations

Solid state far FTIR spectroscopic measurements were performed using a Perkin Elmer 2000 spectrophotometer using the diffuse reflection technique. The spectra were recorded by summing 1000 scans. Far FTIR spectra of triphenylphosphineoxide as well as $CuCl_2[(C_6H_5)_3PO]_2$ from 710 cm^{-1} to 10 cm^{-1} are given in Figure 1.

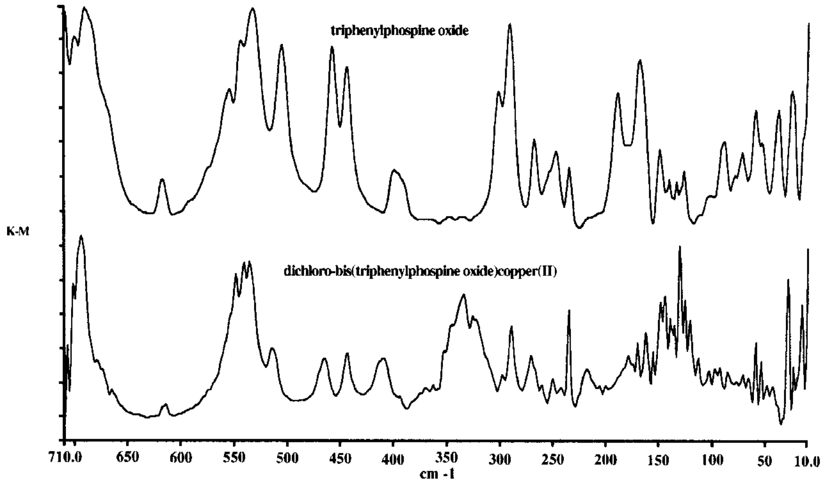

FIGURE 1 Far FTIR spectra of Triphenylphosphine oxide and $CuCl_2[(C_6H_5)_3PO]_2$

Additionally, the substrate and the triphenylphosphineoxide ligand have been measured by mid-range FTIR spectroscopy using KBr pellets. The spectra were recorded with a Perkin Elmer 16 PC spectrophotometer summing 64 scans (see Figure 2).

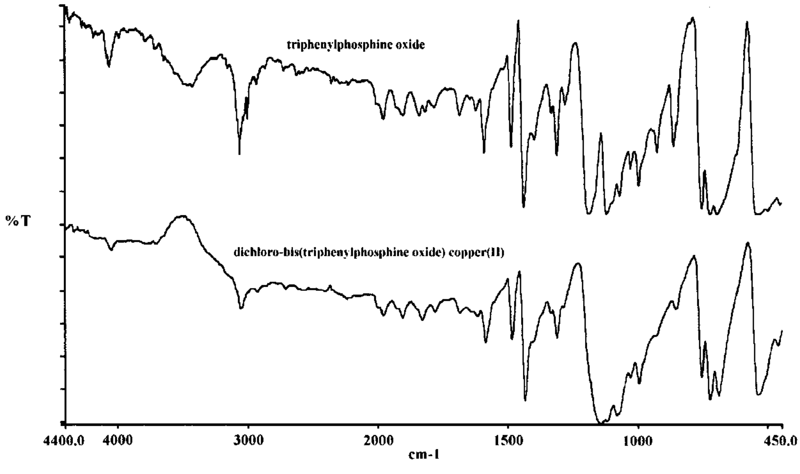

FIGURE 2 Mid FTIR spectra of Triphenylphosphine oxide and $CuCl_2[(C_6H_5)_3PO]_2$

TABLE IV Electronic absorptions of $CuCl_2[(C_6H_5)_3PO]_2$.

wavelength range [nm]	*spectroscopic features*
221	small sharp peak on the shoulder of a very strong peak lower than 190 nm
263	very sharp peak with a shoulder at 270 nm, very high intensity
305	sharp peak, high intensity
456	sharp peak, medium intensity
900	broad peak, low intensity

The electronic spectrum was recorded with a Perkin Elmer Lambda 15 spectrophotometer in the range 900–190 nm using acetonitrile as solvent. The sample shows a very broad peak of low absorption intensity around 900 nm and an intense and sharp peak at 456 nm. The spectroscopic features in the region below 400 nm were resolved only by further diluting the solution. Data for the elctronic absorption spectrum are given in Table IV.

Quantumchemical Calculations

The structure determined by our single crystal X-ray diffraction study was used for quantumchemical calculations performed on a SGI Power Challenge L with four R8000 processors. Due to the fact that $Cu[R_3PO]_2Cl_2$ with R = phenyl (compound 1) is a large system for quantumchemical treatment, analogous complexes with R = methyl (compound 2) and hydrogen (compound 3) have been treated first. A geometry optimization as well as the calculation of spectroscopic features has been performed at DFT level using the Gaussian 94 package[9] for the core of the molecule, *i.e.*, the atoms of the copper coordination centre, using compound 3 as a model for compound 1. For the optimization we used the Becke3 method[10] with Lee, Yang and Parr correlation correction,[11] the 6 - 31 G* basis set for the C, O, P and Cl atoms and the cu-ecp-mdf[12] basis set for the Cu atom. The electronic spectra have been calculated using the semiempirical ZINDO/1 method (HyperChem™,[13]). The vibrational spectrum for the core of the $CuCl_2[(C_6H_5)_3PO]_2$ molecule was calculated semi-empirically as well as by DFT using the smaller STO3-G* basis set. Electron density calculations of the molecular orbitals at DFT and EH levels yielded very different results for compounds 1–3, so no further predictions can be made. Only the electron configuration of the central copper atom can be determined using the geometrically and electronically analogous model compound 3 yielding an electron configuration of [Ne] $3s^2$ $3p^6$ $3d^{9,5}$ $4s^{0,5}$, which is well known for tetrahedrally coordinated copper(II) complexes.

RESULTS AND DISCUSSION

Dichloro*bis*(triphenyphosphineoxide)copper(II) crystallizes in space group F*dd*2, the molecules having point symmetry 2. Cu is surrounded by two O and Cl atoms, which form a distorted tetrahedron. Most tetrahedral copper(II) complexes are distorted toward square planar coordination by compression of the tetrahedron along one of the 4-fold inversion axes. Compression along the 2-fold axis in this compound would lead to O-Cu-O and Cl-Cu-Cl angles larger than 109° and to distortion toward a *trans*-planar complex. In $CuCl_2[(C_6H_5)_3PO]_2$ these two angles are 89.7(2)° and 104.3(1)°, which causes an elongation of the tetrahedron.

The dihedral angle between the O-Cu-O and Cl-Cu-Cl planes of 71.4(1)° indicates a twist in the undistorted tetrahedron leading to a flattened tetrahedron (*cis*-planar coordination). The arrangement of the Cu-O-P atoms is not linear [5] but bent (148.5(2)°), the atom P slightly deviating from the O-Cu-O plane (0.14(1) Å). Similar results where found for the abovementioned tetranuclear species so that the the out of plane position of P appears not to be due to coordinating the mononuclear species *via* the oxo bridge to a tetranuclear compound.

A view of the molecule is shown in Figure 3, and the packing arrangement of the molecules in the unit cell is shown in Figure 4.

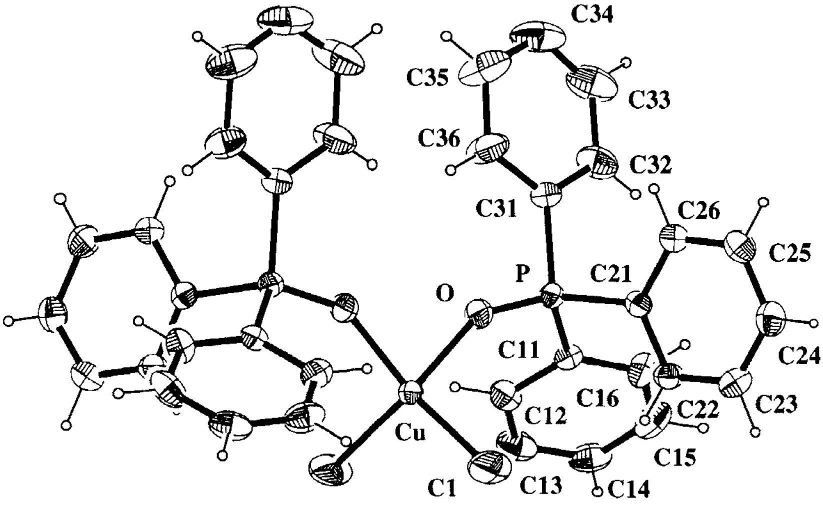

FIGURE 3 ORTEP plot (30% ellipsoids) of $CuCl_2[C_6H_5)_3PO]_2$.

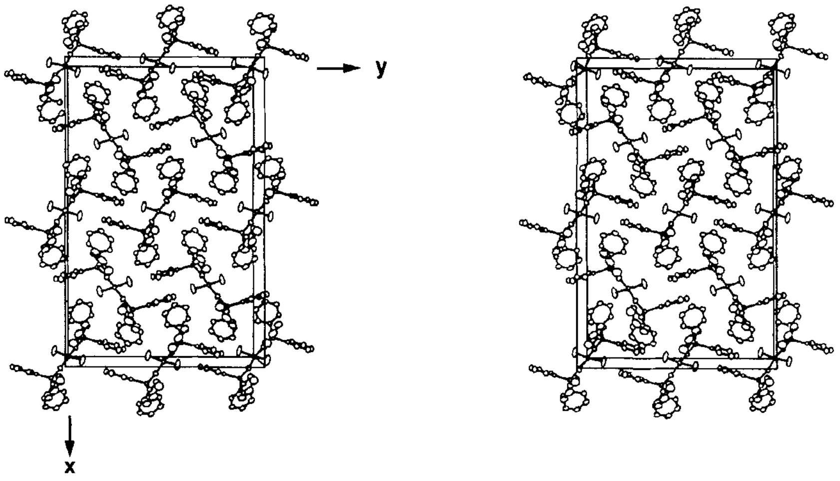

FIGURE 4 Stereographic packing diagram of $CuCl_2[(C_6H_5)_3PO]_2$. View direction down z.

Assignment of vibrational modes is derived from a vibrational analysis performed on model compound 3, yielding sufficiently accurate results for the motion of the core of $CuCl_2[(C_6H_5)_3PO]_2$, *i.e.*, neglecting the phenyl rings and their vibrational modes. Modes below 112 cm^{-1} are mostly due to lattice vibrations of the whole molecule. The absorption at 130 cm^{-1} can be assigned to a deformation of the tetrahedron around the copper coordination centre due to an in-phase shortening of one O-Cu bond and the elongation of the other, as well as an in-plane movement of the copper in the Cl-Cu-Cl plane in the opposite direction as both chlorine atoms are moving in-phase. The vibration at 235 cm^{-1} shows a deformation of the coordination tetrahedron around the copper atom due to an in-phase elongation of one Cu-O and shortening of the other Cu-O bond as well as a movement of the central copper atom in a direction perpendicular to the O-Cu-O plane. The absorptions at 271 cm^{-1} and 289 cm^{-1} are due to in-plane bending motions of the Cl-Cu bonds in phase. The in-phase stretching vibration of both Cu-Cl bonds yields the absorption at 334 cm^{-1}. The very strong absorption around 536 cm^{-1} is due to motion of the P atom in a plane perpendicular to the O-P axis. The two prominent peaks in the mid IR region at 1117 cm^{-1} and 1143 cm^{-1} are due to stretching of the two O-P bonds.

The electronic spectrum of $Cu[(C_6H_5)_3PO]_2Cl_2$ was calculated using the ZINDO/1 method (CI). For the configuration interaction three occupied and three unoccupied molecular orbitals have been chosen yielding 18 configurations. Only a few electronic transitions give an oscillator strength corresponding to a non-forbidden electronic transition. The calculation yields two electronic transitions below the experimental range of 900-190 nm at 130 nm and 140 nm with spin multiplicity 2. We observed at 221 nm a shoulder of a very strong peak below 190 nm, and calculated an extinction maximum of a very strong peak at 143 nm, which might match the experimental result. Additionally, we could calculate strongly absorbing electronic transitions at 266.5 nm with an oscillator strength of 0.157 (which match with the observed maximum at 263 nm) and 268.5 nm with an oscillator strength of 0.126 (which match the observed shoulder at 270 nm). The observed peaks at 305, 456 and around 900 nm might belong to electronically forbidden, but vibrationally allowed transitions (for instance d-d transitions in metals). That is why they could not be calculated. All calculated electronic transitions mentioned above have a spin multiplicity of 2, yielding another singulet state. The oscillator strength is proportional to the integrated spectral absorption.

Supplementary Material

Further details regarding hydrogen coordinates and isotropic displacement parameters, anisotropic displacement parameters, observed and calculated structure factors and least-squares planes data are available from the authors upon request.

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