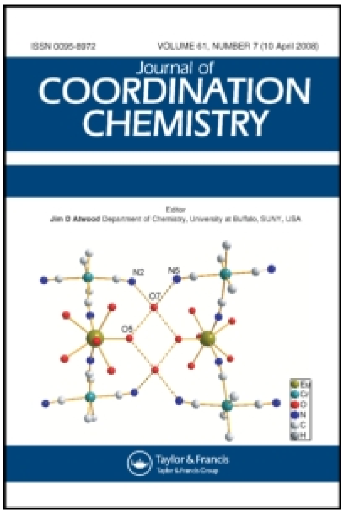

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A luminescent copper(I) bromide complex chelated with 4,5-*bis*(diphenylphosphano)-9,9-dimethyl-xanthene

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The 1 : 1 molar-ratio reaction between copper(I) bromide and 4,5-*bis*(diphenylphosphano)-9,9-dimethyl-xanthene (xantphos) in acetonitrile results in the formation of [CuBr(xantphos)], which displays luminescent emission at room temperature. The molecular structure of the complex, established by single-crystal X-ray diffraction, features a trigonal planar geometry around the metal center, with the diphosphane acting as a chelate. The high rigidity and steric requirements of the xanthene unit rationalize the unusual coordination number of Cu^I.

Keywords: Copper(I) bromide; Xantphos; Crystal structure; Luminescence

1. Introduction

The stereochemistry of copper(I) complexes is dominated by four-coordination, whereas three-coordinate species are by far less common. In general, primary control over the coordination number of these compounds can be achieved by the choice of ligands having specific geometrical and/or electronic characteristics. Indeed, according to our hitherto experience with the use of simple triarylphosphanes in the synthesis of mixed-ligand copper(I) halide complexes bearing heterocyclic thiones as co-ligands, the bulkiness of the phosphane strongly influences the overall molecular topology of the compounds formed. Thus, for example, four-coordination is preferred when small cone angle triarylphosphanes like triphenyl-, *tri*-m-tolyl-, and *tri*-p-tolyl-phosphane are used, against the trigonal planar coordination environment observed in complexes formed by the bulkier *tri*-o-tolylphosphane [1]. In this respect, flexible oligomethylene-backboned diphosphanes of type $Ph_2P(CH_2)_nPPh_2$, but interestingly also the rigid 1,2-*bis*(diphenylphosphanyl)benzene, were found to resemble the aforementioned small cone angle triarylphosphanes, exclusively forming four-coordinate species, independent of the bridging or chelating binding mode adopted in each case [2, 3].

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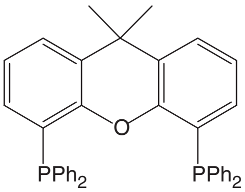

Scheme 1. The rigid diphosphane xantphos.

Considering further sterically demanding bidentate P-donor ligands, the extended xantphos family of diphos ligands, initially developed for the use as fine-tuned ligands for metal complexes with specialized catalytic properties [4, 5], is expected to be capable of exerting an influence on the coordination number of monovalent Group 11 metal complexes. Thus, we recently included 4,5-*bis*(diphenylphosphano)-9,9-dimethyl-xanthene (xantphos, scheme 1), the parent member of the above family, in our systematic structural studies on mixed-ligand copper(I) and silver(I) halide complexes. Note that, although xantphos has already been extensively used as a ligand in diverse metal complexes and several types of coordination modes have been established over the years [6], there were few structures of Group 11 compounds known, namely $[(AuX)_2(\mu\text{-xantphos})]$ ($X = Cl, NO_3$) and $[Au(xantphos)_2]SbF_6$, with the xantphos unit adopting the bidentate bridging and chelating coordination mode, respectively [7]. Nevertheless, despite its more or less configurationally inflexible heteroarene skeleton, xantphos proved to be best designed to chelate to copper(I) and silver(I) both in a tetrahedral or trigonal coordination environment, with the coordination number apparently being determined by the nature of the co-ligands present. In particular, we reported on the synthesis and characterization of some tetrahedral complexes of general formula [CuBr(xantphos)(thione)] obtained by treatment of a CuBr/xantphos intermediate of unknown structure with several neutral heterocyclic thioamides [8]. More recently we were able to isolate and structurally characterize [AgBr(xantphos)] as a monomer with a roughly trigonal environment around the metal centre, which has been further used as an intermediate for the synthesis of tetrahedrally coordinated mixed-ligand complexes of type [AgBr(xantphos)(thione)] [9]. It should be pointed out, however, that analogous CuX/diphos and AgX/diphos compounds formed by the rigid 1,2-*bis*(diphenylphosphanyl)benzene (dppbz) are dimers, $[(dppbz)M(\mu\text{-}X)_2M(dppbz)]$, featuring two phosphane-chelated metal centers doubly bridged by halide ligands [3].

To gain better insight into the interplay between ligand characteristics (bulkiness, rigidity) and the structural diversity observed in the above class of complexes, we now wish to report on the chelation of xantphos to CuBr resulting in the formation of a stable monomeric three-coordinate complex.

2. Experimental section

2.1. *Materials and instrumentation*

Commercially available copper(I) bromide, and 4,5-*bis*(diphenylphosphano)-9,9-dimethyl-xanthene (Aldrich) were recrystallized from hot ethanol prior to use. All solvents were purified by standard methods and allowed to stand over molecular sieves.

The infrared spectrum in the region 4000–250 cm^{-1} was recorded with a Perkin-Elmer 1430 spectrophotometer. The electronic absorption spectrum was measured with a Perkin-Elmer-Hitachi 200 spectrophotometer, while a Hitachi F-700 fluorescence spectrophotometer was used to obtain the emission spectrum. The ^1H NMR spectrum was recorded on a Brucker AM 300 spectrometer at 25°C with positive chemical shifts given downfield from TMS. The ^{31}P NMR spectrum was recorded on a Brucker 400 spectrometer and is referenced to external 85% H_3PO_4. The melting point of the compound was measured in an open tube with a STUART scientific instrument. Molar conductivity, magnetic susceptibility and elemental analysis for carbon and hydrogen were performed as described previously [10].

2.2. *Crystal structure determination*

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of the acetonitrile solution of the complex at room temperature. X-ray diffraction data were collected on an Oxford Xcalibur3 CCD diffractometer with graphite monochromated Mo-Kα radiation. The data collection and reduction were carried out with the CrysAlis CCD [11] and CrysAlis RED [12] software, respectively. For structure solution and refinement (direct methods, full matrix least-square on F^2, anisotropic atomic displacement parameters for all non-hydrogen atoms) SHELXTL97 [13] by Bruker was used (table 1).

Table 1. Crystal Data and Structure Refinement for [CuBr(xantphos)].

Molecular formula	$C_{39}H_{32}BrCuOP_2$
Formula weight	722.04
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P1$
a (Å)	9.816(2)
b (Å)	10.014(2)
c (Å)	10.463(2)
α (°)	104.85(3)
β (°)	103.32(3)
γ (°)	111.52(2)
Volume (Å^3)	805.3(3)
Z	1
Density (calculated, $g\,cm^{-3}$)	1.489
Absorpt. Coefficient, μ (mm^{-1})	2.049
$F(000)$	368
Crystal size (mm^3)	0.1 × 0.2 × 0.2
Theta range for data collection (°)	3.25–25.29
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-12 \le l \le 12$
Reflections collected	9868
Independent reflections	5173 ($R_{int} = 0.068$)
Completeness	99.8%
Data/restraints/parameters	5173/3/399
Refinement method	Full-matrix least squares on F^2
Goodness-of-fit on F^2	0.972
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.069$, $wR_2 = 0.160$
R indices (all data)	$R_1 = 0.085$, $wR_2 = 0.170$
Final weighting scheme	$1/[\sigma^2(F_o^2) + (0.10220P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
Largest diff peak and hole (e Å^{-3})	2.172 and −0.676

2.3. *Synthesis of [CuBr(xantphos)] • 2MeCN*

To a suspension of 0.5 mmol (71.7 mg) of copper(I) bromide in 30 mL of dry acetonitrile, 289.3 mg (0.5 mmol) of 4,5-*bis*(diphenylphosphano)-9,9-dimethyl-xanthene was added and the mixture was stirred for 2 h at 50°C. The small amount of a white precipitate formed during that time was filtered off and the resulting clear solution was left to evaporate at ambient temperature. The white microcrystalline solid, which deposited upon standing for several days, was filtered off and dried *in vacuo*, yield 326 mg (90%), m.p. 325°C. Anal. Calcd for $C_{41}H_{38}BrCuN_2OP_2$(%): C, 64.71; H, 4.81; N, 3.21. Found: C, 64.22; H, 4.76; N, 3.48. IR (cm^{-1}): 3437 m, 3052 w, 2958 w, 1479 w, 1434 m, 1403 s, 1255 m, 1097 w, 874 w, 751 m, 696 m, 513 m, 503 m, 463 w. Uv-Vis (λ_{max}, $\log \varepsilon$), ($CHCl_3$): 247 (4.35), 276 (4.09). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.52–7.55 (d, 2H, $H^{1,8}$), 7.14–7.45 (m, 20 H, PPh_2), 7.1 (dd, 2H, $H^{2,7}$), 6.56 (d, 2H, $H^{3,6}$), 1.68 (s, 6H, H_3C). ^{31}P-NMR ($CDCl_3$): −17.78 ppm. The compound is moderately soluble in acetonitrile and only slightly soluble in non-polar solvents such as chloroform or acetone. Its solutions in common organic solvents are non-conducting.

3. Results and discussion

3.1. *General aspects*

The structural motifs usually displayed by copper(I) and silver(I) halide complexes bearing chelating rigid diphosphanes in a tetrahedral coordination environment are either discrete monomers, or dimers containing the $M(\mu_2\text{-}X)_2M$ core. Attempts to chelate copper(I) with *cis*-1,2-*bis*(diphenylphosphano)ethene (*cis*-dppen) and 1,2-*bis*(diphenylphosphano)benzene (dppbz) gave both of the above mentioned structural types for each of these two rigid diphosphanes [14, 3]. Moreover, the preference of a rigid bidentate ligand for a certain coordination mode (chelating or bridging) depends, to a significant degree, on its "bite angle", and chelation is normally favoured for bite angles close to those required by the geometry of the coordination polyhedron being formed. Consequently, the ability of the above diphosphanes to span tetrahedral sites under formation of fairly constrained P–M–P angles having values far from their quite short natural bite angles, should be connected with the extraordinary versatility of the d^{10} metal ion. With this in mind, the potential of xantphos to chelate monovalent Group 11 metal halides, either in a tetrahedral or trigonal planar environment can be easily explained, and in addition, steric demands on the part of the ligands may be responsible for the adoption of a distinct coordination number in each case. Indeed, treatment of CuX or AgX with xantphos always results in formation of a three-coordinate chelate, independent of the ratio of the phosphane, whereas addition of one equivalent of a heterocyclic thione to solutions of the compounds [MX(xantphos)] causes increase of the coordination number, leading to the formation of four-coordinate xantphos/thione mixed-ligand species. It is obvious that four-coordination by dimerization of [MX(xantphos)] species to $[M(\mu\text{-}X)(xantphos)]_2$, as in the case of their cis-dppen or dppbz counterparts, cannot be achieved, in all probability for steric reasons.

3.2. *Spectroscopy*

The room-temperature ^{1}H NMR spectrum of the compound, recorded in deuterated chloroform, is dominated by the presence of a typical set of multiplets in the region of $\delta = 7.40$–7.20 ppm attributed to the phenyl resonances of the xantphos ligand. Upon coordination the complex multiplet assigned to the PPh$_2$ units undergoes splitting due to the upfield shift of the ortho-positioned protons by ca 0.25 ppm. The corresponding shifts of the H^6, H^7 and H^8 protons, as well as of the methyl-protons are in the same direction but of clearly smaller magnitude (less than 0.1 ppm). The ^{31}P NMR spectrum shows a single resonance at -17.78 ppm, indicating the presence of two equivalent phosphorus atoms. The very small shift of this resonance relative to un-coordinated xantphos is in accord with the fact that coordination to copper(I) is not expected to cause large shifts [15].

The electronic absorption spectrum recorded in chloroform at room temperature, shows two intense broad bands with maxima at 247 and 276 nm. With reference to the absorption spectrum of the uncoordinated xantphos, the first one can be attributed to intraligand $\pi^* \leftarrow \pi$ transitions on the phenyl groups of the phosphane ligand whereby the lower energy band, can be considered as a phosphane-originating MLCT transition [16, 17].

Room-temperature photoexitation of a solid sample of the compound into consideration at $\lambda = 350$ nm produces an intense broad emission band with peak maximum at $\lambda = 502$ nm and a shoulder at ca 420 nm (figure 1). This emission cannot be considered as one of pure intra-ligand origin, because of its significant red shift relative to the solid-state r.t. emission spectrum of free xantphos that consists of a broad band centered around 465 nm. On the other hand, the observation that the analogous compound [AgBr(xantphos)] also intensively emits at the same energy does not appear to be compatible with a metal-to-ligand charge-transfer excited state only. Thus, we tentatively assign the photoluminescence as having mixed character between MLCT

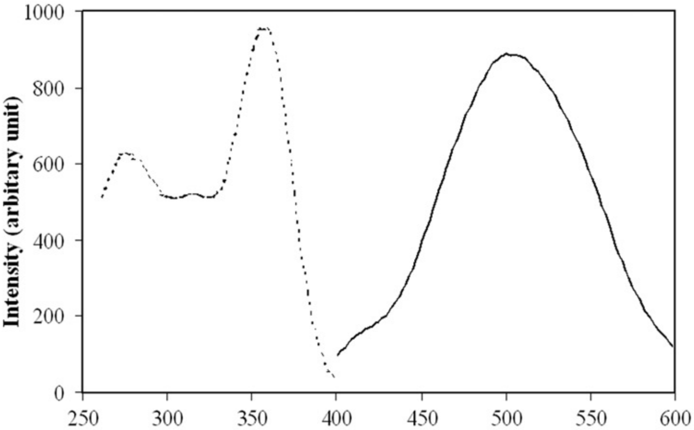

Figure 1. Room-temperature solid-state excitation (dashed line, $\lambda_{em} = 502$ nm) and emission (solid line, $\lambda_{ex} = 350$ nm) spectra of [CuBr(xantphos)]2MeCN.

[d(Cu → π*(xantphos)] and IL (π → π*) transitions associated with the phenyl rings of xantphos.

3.3. *Crystal structure*

The X-ray crystal structure of [CuBr(xantphos)] corroborates the spectroscopic results discussed above. Table 2 lists the distances and angles around the metal center. Despite its almost symmetric character with respect to the C(7) ··· O(1) ··· Cu(1) plane, the complex crystallizes in the triclinic space group *P*1 (in contrast with the space group $P2_1/m$ of [AgBr(xantphos)] [9]). This is attributed to crystal packing since the absolute structure determination (Flack parameter) is correct. As shown in figure 2, the copper(I) centre is three-coordinate and deviates by only 0.235(1) Å from the plane defined by the P atoms of the chelating xantphos unit and the bromine atom.

Table 2. Selected bond lengths (Å) and angles (°) for [CuBr(xantphos)].

Cu(1)–P(1)	2.254(3)	P(1)–Cu(1)–P(2)	117.04(10)
Cu(1)–P(2)	2.255(3)	P(1)–Cu(1)–Br(1)	118.98(8)
Cu(1)–Br(1)	2.341(2)	P(2)–Cu(1)–Br(1)	120.86(8)

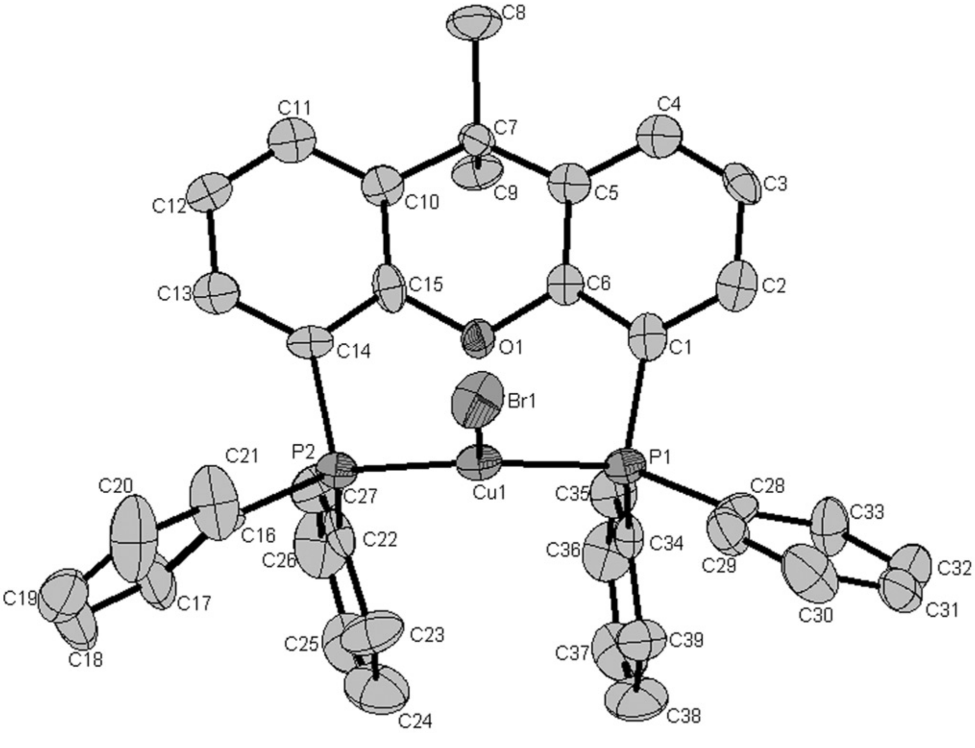

Figure 2. A view of [CuBr(xantphos)] with atom labels. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Interestingly, the single-crystal analysis indicates no acetonitrile molecule, neither coordinated nor trapped in the crystal lattice.

The angular deviations from the ideal trigonal value of 120 are quite small. Still, chelation of xantphos apparently requires some distortion of the diphosphane backbone. In fact, the $P \cdots P$ distance of 4.045(1) Å for the free xantphos appears shortened to a value of 3.845(4) Å, accompanied by a respective adaptation of the folding of the central ring along the $Me_2C \cdots O$ plane (143.95° *vs.* 156.58° in the free ligand). The phenyl rings on each phosphorus are nearly perpendicular to each other (103° and 104°). However, the C(22)–C(27) and C(34)–C(39) phenyl rings have their planes in an almost parallel arrangement with 3.61–3.85 Å π-stacking interaction between them. No intermolecular π-stacking, namely among the C(16)–C(21) and/or C(28)–C(33) phenyl rings is observed. Also, the $Cu \cdots O$ distance is found at 2.865(8) Å, and cannot be considered as bonding. We count the $Cu \cdots H$–C(8) for the strongest intermolecular interaction with a distance of 2.794(1) Å and angle 108.5(9)°. The two strongest peaks of residual electron intensity are found about 0.2 Å adjacently to Br(1), but one cannot apply a split model for this atomic position, due to bad anisotropic refinement.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited in the Cambridge Crystallographic Data Centre, CCDC 644734. Copies can be obtained free of charge at www.code.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (intrnat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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