

Complexes of Copper and Gold with Phosphorus–Sulfur Bidentate Ligands

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Abstract

Copper(II) salts react with the bidentate hybrid ligands 1-thiophenyl-2-diphenylphosphinoethane (PSPH) and 1-thioethyl-2-diphenylphosphinoethane (PSEt) to yield copper(I) and/or copper(II) complexes of composition $[\text{Cu}(\text{PSR})_2]Y$ and $[\text{Cu}(\text{OPSR})_2]Y_2$ ($Y = \text{ClO}_4, \text{BF}_4$; OPSR = phosphino-oxide of the PSR ligand). A mixed-valence species $\text{Cu}^{\text{II}}(\text{OPSEt})_2Y_2 \cdot \text{Cu}^{\text{I}}(\text{PSR})_2Y$ has been isolated. The interaction of the PSR ligands with silver(I) and gold(III) salts has been also studied and gold(I) derivatives of the type $[\text{AuX}(\text{PSR})]$ have been isolated.

Introduction

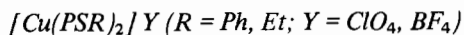
The coordinating properties of hybrid Group V and VI donor ligands have been the object of considerable interest, mostly in connection with studies on the factors dictating the stabilization of unusual coordination numbers and oxidation states of transition metal ions. Previous papers from our laboratory described the complexes formed by some simple phosphorus–sulfur bidentate ligands of the type $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{SR}$ (PSR; R = Ph: PSPH, R = Et: PSEt) with a number of d^8 metal-ions, such as nickel(II) [1], platinum(II) and palladium(II) [2] and rhodium(I) and iridium(I) [3]. Now we report an investigation on the complexes formed by the above PSR ligands with IB Group metals. It should be noted that phosphine ligands usually react with copper(II) salts to give either copper(I) phosphino-derivatives or copper(II) complexes with the corresponding phosphine-oxides, formed upon oxidation of the ligands [4]. Only very few examples are known of phosphino-complexes of copper(II), most of them, significantly, with hybrid ligands [5], but the properties of the ligands necessary for stabilizing the oxidation state II of copper are far from fully understood.

Experimental

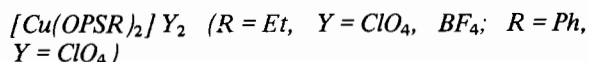
The PSR ligands were prepared as described previously [1a]; the corresponding phosphine-oxides OPSR were prepared from the PSR ligands, by treat-

ment with KI and H_2O_2 , following a general procedure for the synthesis of phosphine-oxides [6].

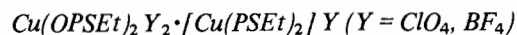
IR and UV–Vis spectra were recorded on Perkin-Elmer 457 and 576 spectrophotometers respectively; ESR spectra on a JEOL PE-3X spectrometer; ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were measured at 24.28 and 60 MHz on a Bruker WP 60 FT instrument. Magnetic measurements were made by Gouy's method. Conductivities were obtained on a Radiometer CDM-3 conductivity bridge.



$\text{CuY}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) was dissolved in ethanol and PSR (2.5 mmol), dissolved in dichloromethane, was added. The initial blue solution turned progressively colorless and white precipitates separated, which could be recrystallized from dichloromethane–ethanol (80–90%).



$\text{CuY}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) was dissolved in 2-propanol and OPSR (2 mmol), dissolved in acetone, was added. By evaporating *in vacuo*, colored solids separated (65–95%).



$\text{CuY}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) was dissolved in ethanol and PSEt (500 mg, 1.8 mmol), dissolved in acetone, was added dropwise, to give a green solution. By addition of 2-propanol, a green solid separated upon concentration *in vacuo* (15–35%).



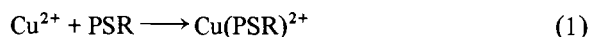
HAuCl_4 (300 mg, 0.8 mmol) was dissolved in 2-propanol and PSEt (440 mg, 1.6 mmol), dissolved in acetone was added. The solution rapidly decolorized and, by concentrating *in vacuo*, yielded a white mass, which was shaken vigorously overnight in 2-propanol, until white crystals formed (65%).

Results and Discussion

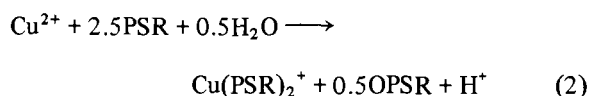
Copper Complexes

The reaction between copper(II) perchlorate or tetrafluoroborate and the ligands PSR leads to the

formation of copper(I) and/or copper(II) derivatives. Alcohol solutions of copper(II) perchlorate turn green upon addition of equimolar amounts of the PSR ligands. The UV-Vis spectra of these solutions exhibit a weak, but detectable shoulder in the 350 nm region, attributable to the diagnostic $S(\sigma) \rightarrow Cu''$ - (d) LMCT transition [7], possibly of an intermediate 1:1 adduct between copper(II) and the ligand, which however cannot be isolated.



Addition of more ligand results in the progressive fading of the green color of the reaction mixtures, with contemporary disappearance of the above absorption and formation of the copper(I) derivatives $[Cu(PSR)_2]^+$ and phosphine-oxide (eqn. (2)).



In the presence of excess copper, pale green solutions are obtained, from which green ($R = Et$) or brown ($R = Ph$) crystals of composition $Cu(OPSR)_2 \cdot Y_2$ are recovered by addition of 2-propanol. The compounds are also prepared by reacting directly the ligands OPSR with the appropriate copper(II) salts. Copper(I) and copper(II) complexes have been fully characterized by elemental analyses, magnetic moment and conductivity measurements (Table I).

The IR spectra (Nujol mull) indicate that the anions Y are not coordinated in the $[Cu(PSR)_2]Y$ complexes, whereas those of $Cu(OPSR)_2(ClO_4)_2$ give evidences of semicoordination. Three distinct peaks are in fact detectable in the $\nu_3(ClO_4^-)$ band region at

1105, 1085 and 1070 cm^{-1} (a strong ν_{PO} absorption is also observed at 1125 cm^{-1}). The tetrafluoroborate-derivatives exhibit an even more complicated spectral pattern in the 1150–950 cm^{-1} region, due to the presence of ν_{PO} and $\nu_3(BF_4^-)$ from coordinated and uncoordinated $^{11}BF_4^-$ and $^{10}BF_4^-$ groupings.

The electronic spectra of $Cu(OPSEt)_2(ClO_4)_2$ are identical in the solid state (Nujol mull) and in solution (dichloromethane). Apart from the broad asymmetric d–d band at 670 nm, a very intense absorption is observed at 430 nm ($\epsilon_M = 7500$), which is appropriate in energy for the diagnostic $S(\sigma) \rightarrow Cu''(d)$ LMCT transition, being the elevated optical density not uncommon for this type of transition [7, 8]. Finally, the benzenoid band at 270 nm displays the characteristic vibrational fine structure, which has been demonstrated to be diagnostic for the presence of $(C_6H_5)PO$ groupings [9].

Another product can be recovered from the reaction mixtures, when an excess of copper(II) is reacted with the ligand PSEt (but not with the related ligand PSPH). Upon addition of 2-propanol, the solutions quickly separated and when concentrated *in vacuo*, a green compound of composition $Cu''(OPSEt)_2Y_2 \cdot Cu'(PSEt)_2Y$ ($Y = ClO_4, BF_4$) was obtained. Magnetic moments of the compounds, once recalculated per copper(II) atom, give typical values (2 BM), while UV-Vis spectra (Nujol mull) are identical with those of the $Cu''(OPSEt)_2Y_2$ chromophores, discussed above. The IR spectra are practically the superposition of those of $Cu(OPSEt)_2Y_2$ and of $[Cu(PSEt)_2]Y$, giving rise to a complicated fingerprint pattern in the 1150–950 cm^{-1} region. Thus, since the melting point of the products are definitely different from those of equimolar mechanical mixtures of the copper(I) and copper(II) constituents, we con-

TABLE I. Analytical and Physical Data

Compound	Color	μ_{eff} (BM) ^a	Analyses ^b
OPSEt	c	d	C, H
OPSPH	c	d	C, H
$Cu_2(OPSEt)_2(PSEt)_2(ClO_4)_3$ ^e	green	1.46	C, H, Cl
$Cu_2(OPSEt)_2(PSEt)_2(BF_3)_3$ ^f	green	1.58	C, H
$Cu(OPSEt)_2(ClO_4)_2$	green	2.06	C, H, Cl
$Cu(OPSEt)_2(BF_4)_2$ ^g	green	2.02	C, H
$Cu(OPSPH)_2(ClO_4)_2$	brown	2.08	C, H, Cl
$Cu(PSEt)_2ClO_4$	c	d	C, H, Cl
$Cu(PSEt)_2BF_4$ ^h	c	d	C, H
$Cu(PSPH)_2ClO_4$	c	d	C, H, Cl
$Cu(PSPH)_2BF_4$	c	d	C, H
$AuCl(PSEt)$ ⁱ	c	d	C, H, Cl

^aAt 20 °C, calc. per Cu atom.

^bWithin 0.3% of theory.

^cColorless.

^dDiamagnetic.

^eBand maximum (nm), in Nujol mull:

265, 300(sh), 430, 650.

^fBand maximum (nm), in Nujol mull: 275, 300(sh), 430, 625; in CH_2Cl_2 (ϵ_M): 265(6700),

420(7500), 670(190).

^gFrom Onsager's equation $\Lambda_0 = \Lambda_e + A\sqrt{N}$, $\Lambda_0 = 101$ and $A = 335$, in nitromethane at 25 °C.

^hFrom Onsager's equation $\Lambda_0 = \Lambda_e + A\sqrt{N}$, $\Lambda_0 = 87$ and $A = 210$ in nitromethane at 25 °C.

ⁱMolecular weight (osmometric) in 1,2-dichloromethane: 511 (calc., 506.8).

clude that $\text{Cu}''(\text{OPSet})_2\text{Y}_2 \cdot \text{Cu}'(\text{PSet})_2\text{Y}$ really are mixed valence complexes, likely of the type **a**, following early classifications [10]. An XPS investigation [11], carried out separately, confirmed that the mixed species behave as double salts, without specific interactions between copper(I) and copper(II).

ESR spectra show, instead, significant differences between $\text{Cu}''(\text{OPSet})_2(\text{BF}_4)_2$ and $\text{Cu}''(\text{OPSet})_2\text{Cu}'(\text{PSet})_2(\text{BF}_4)_3$. In fact, whereas the polycrystalline ESR spectra of the copper(II) derivative are characterized by a g_{\parallel} value of 2.220 and by a small anisotropy of the g_{\perp} value (2.089), for the mixed-valence species the pattern of the ESR parameters are apparently different, in the sense that g_{\parallel} is found to increase up to 2.269 and a noticeable anisotropy of g_{\perp} is observed. The spectrum shows three well-separated signals, which allow one to determine the three g values (Fig. 1).

Differences between the above ESR data can be explained assuming geometrical distortion of the $\text{Cu}(\text{OPSet})_2(\text{BF}_4)_2$ chromophore when in the mixed species, probably induced by the presence in the crystal of the tetrahedral $[\text{Cu}(\text{PSet})_2]^+$ cation. Host lattice-induced changes of geometry for tetragonal copper(II) complexes are indeed well-documented. For example, a closely related mixed-valence derivative of copper, containing the dithioetheral ligand $\text{CH}_3\text{S}(\text{CH}_2)_2\text{SCH}_3$ (DTH), has been reported [12], of composition $[\text{Cu}_3(\text{DTH})_6]\text{Y}_4$, for which X-ray evidences indicate a strongly distorted geometry for copper(II).

Attempts to obtain crystals of $\text{Cu}(\text{OPSet})_2 \cdot \text{Cu}(\text{PSet})_2\text{Y}_3$, suitable for an X-ray determination of the structure, were unsuccessful, since common organic solvents cause fractionation of the mixed species within minutes.

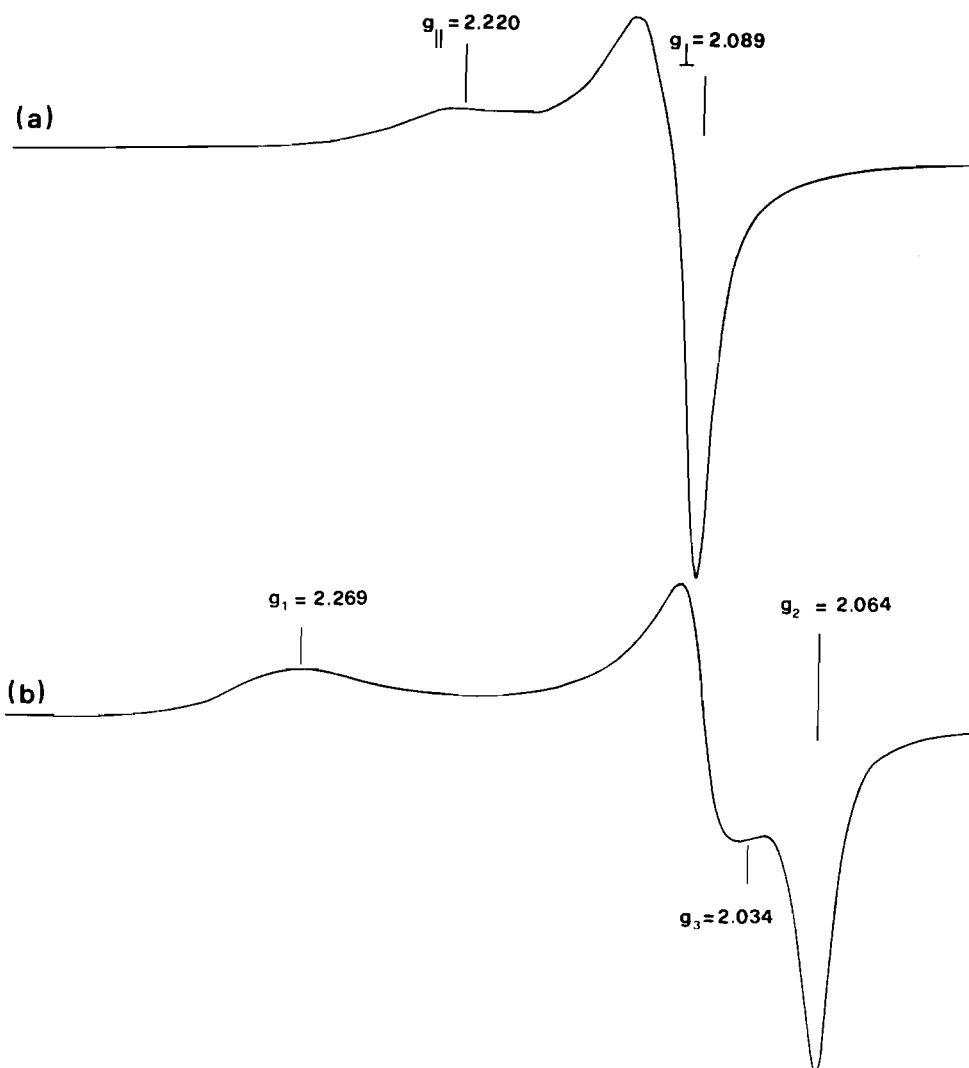
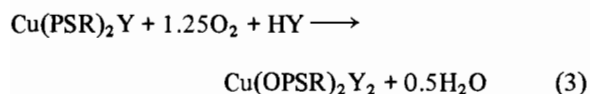


Fig. 1. Polycrystalline ESR spectra of: (a) $\text{Cu}(\text{OPSet})_2(\text{BF}_4)_2$; (b) $\text{Cu}(\text{OPSet})_2(\text{BF}_4)_2 \cdot \text{Cu}(\text{PSet})_2\text{BF}_4$.

The copper(I) derivatives $[\text{Cu}(\text{PSR})_2]\text{Y}$ are fairly stable in air in the solid state, but once dissolved in ethanol and other polar solvents, slowly take up oxygen under room conditions, giving, with time, green solutions containing the $\text{Cu}(\text{OPSEt})_2\text{Y}_2$ chromophores (eqn. (3)).



Gold Complexes

No solid products could be isolated from the reaction between the PSR ligands and ethanolic AgBF_4 , whereas HAuCl_4 readily reacts with the above ligands giving the colorless gold(I) complexes $\text{AuCl}(\text{PSR})$. Only the complex containing PSEt has been isolated in the solid state, being the PSpH-derivative a tenacious colorless oil.

Molecular weight measurements and conductivity data (Table I) indicate that $[\text{AuCl}(\text{PSEt})]$ is monomeric and non-electrolyte in solution. The chelate nature of the ligand (hence the 3-coordinate nature of the metal) has been inferred by the proton NMR spectrum, in CDCl_3 , which exhibit, among other signals, a diagnostic, single resonance at 2.75 ppm, due to the methylene protons of the alkyl chain of the ligand. Equivalence (or quasi-equivalence) of the chain-protons occurs upon coordination of the PSR ligands through both sulfur and phosphorus, whereas an A_2B_2 pattern is usually found for the CH_2CH_2 protons in free or monodentate ligands.

Acknowledgment

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