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The Dithiosquarato Cuprate and the Dithiosquarato Palladate Ions: Single Crystal ESR Study and Crystallographic Investigations

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Abstract

The crystal structure of $[Pd(dtsq)_2](Ph_4P)_2$ has been determined and the single crystal ESR study of the $[(dtsq)_2Cu(II)]^{2-}$ ion has been performed in $[(dtsq)_2Cu](Ph_4P)_2$ and in doped $[Pd(dtsq)_2](Ph_4P)_2$. It is shown that the physicochemical properties are strongly dependent upon the nature of the counterion: the presence of the voluminous Ph_4P^+ cation increases the intermetallic distance and precludes the interstack interactions which have been previously observed with K^+ as counterion.

Introduction

Crystals composed of molecular ions and exhibiting strongly anisotropic behaviours are currently of great experimental and theoretical interest [1]. Planar complexes, for example, can form one dimensional systems consisting of stacks of strongly interacting metal atoms and may present interesting conduction properties. In this context, 1,2-cyclobutadiene-3,4 dithiolate (the dianion of *cis*-dithiosquaric acid: $(dtsq)^{2-}$) is an attractive ligand since it consists of planar, highly delocalized molecules allowing close stacking. Molecular architectures related to those observed in bis(oxalato)platinates [2] or in the dithiolene compounds [3] should be expected. Some transition metal complexes of dithiosquaric acid were previously described by Coucouvanis *et al.* [4]. We report the X-ray structural investigation of $[Pd(dtsq)_2](Ph_4P)_2$ and the physicochemical study of copper(II) and palladium(II) compounds obtained from this ligand and we will examine the incidence of the nature of the counterion on the properties of these materials.

Experimental

Synthesis

Potassium dithiosquarate was prepared according to Maaks [5]. The syntheses of the complexes were performed as described elsewhere [4, 6, 7]. Cocrystallization of $[Pd(dtsq)_2](Ph_4P)_2$ and a small amount of $[Cu(dtsq)_2](Ph_4P)_2$ leads to the isolation of copper(II) complex units in an isostructural matrix of palladium(II) complex.

Physical Measurements

Conductivity

Powder conductivities were determined on compressed pellets with a Wayne Ker Automatic Bridge B 605. The pellets were pressed and their resistance directly measured in a 'conductivity press' by applying a force of 100 Kg on 3 mm-diameter pistons moving in a glass capillary tube.

Electron Spin Resonance

ESR spectra were recorded at room temperature on a Varian E-9 spectrometer (100 KHz field modulation, X-band) equipped with a goniometer which has been previously described [9]. The angular dependence of the spectra was analyzed by using a Hamiltonian $\mathcal{H}$ which took into account the electronic ($\tilde{g}$) and nuclear Zeeman effects and the quadrupolar ($\tilde{P}$) and magnetic ($\tilde{T}$) hyperfine interactions with $^{63/65}Cu$ (^{63}Cu: natural abundance 69%, $I = 3/2$, $g_n = 1.4804$; ^{65}Cu: natural abundance 31%, $I = 3/2$, $g_n = 1.5859$)

$$\mathcal{H} = \beta H S \tilde{g} h - g_n \beta_n H I + S \tilde{T} I + I \tilde{P} I$$

where h is an unit vector aligned along the magnetic field direction, S and I correspond to the electron and nuclear spin respectively. The various tensors were obtained using a second order perturbation calculation together with a minimization subroutine [10].

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TABLE I. *Crystal Structure of* $[Pd(dtsq)_2](Ph_4P)_2$: *Summary of Crystal Data, Intensity Measurement and Structure Refinement*

Formula	$C_4O_2S_2Pd_{0.5}/C_{24}H_{20}P$
Molecular weight	536.8
Crystal system	monoclinic
Space group	$P2_1/n$
Crystal size (mm)	0.10 × 0.18 × 0.28
Unit cell determination	least-squares fit from 20 reflections (21° < 2θ < 28°)
a (Å)	11.037(2)
b (Å)	15.314(2)
c (Å)	14.621(2)
β (°)	94.62(1)
Z	4
D_{calc} (g cm^{-3})	1.447
$F(000)$	1096
μ (cm^{-1})	6.429
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.528
h, k, l range	−11,11 0,16 0,15
No. measured reflections	3325
Max. and min. (A)*	1.119, 1.064
Criterium for observed reflections	$\|F\| > 4\sigma(F)$ and $\|F\| > 8$
No. observed reflections	2143
Refinement	two blocks
No. parameters	305
Weighting scheme	$w(F) = 1$
Coordinates of hydrogen atoms	calculated
Max. and min. $\Delta\rho$(eÅ^{-3})	0.42, −0.79
R	0.045

Crystallography

Experimental data and refinement conditions for the structure determination of $C_4O_2S_2Pd_{0.5}/C_{24}H_{20}P$ are summarized in Table I. (Philips PW1100 diffractometer, $T = 294$ K, graphite monochromated Mo Kα ($\lambda = 0.71069$ Å), $\omega/2\theta$ scans, ω-scan angle 1.2°, absorption correction by Gaussian grid integration on grid of 12 × 12 × 12 points, structures solved by MULTAN 80 [11].) No secondary-extinction correction. Atomic scattering factors and anomalous dispersion terms for S, P and Pd atoms were taken from the International Tables for X-Ray Crystallography [12]. All calculations were performed with a local version of XRAY 76 [13] and ORTEP II [14].

Results

Reaction of the dithiosquarate ligand with either palladium or copper salts lead to crystalline products of general formulation $[M(dtsq)_2]X_2$ (where M = Pd, Cu and X = K, Ph_4P). However, it may be underlined that for copper complexes only the tetraphenylphosphonium salt may be obtained. In all other cases, a reduction of the metal by the sulfur ligand occurred. We have observed the same phenomenon when Pt(IV) or Pd(IV) salts react with the dithiosquarate ligand.

Crystallography

The bis(dithiosquarato)palladium anion in $C_4O_2S_2Pd_{0.5}/C_{24}H_{20}P$ is totally planar and the palladium atom is coordinated in a square planar fashion to four sulfur atoms from two ligands. The metal atom is located in the special position $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Relevant interatomic distances (Å) and selected bond angles (°) are listed in Table II, according to the atom numbering of Fig. 1. This structure is isotypic with that of the copper complex [7].

TABLE II. Crystal Structure of $[Pd(dtsq)_2](Ph_4P)_2$: Relevant Interatomic Distances (Å) and Bond Angles (°)[a]

Pd–S(1)	2.337(2)
Pd–S(2)	2.333(2)
S(1)–C(101)	1.708(8)
S(2)–C(102)	1.714(8)
O(1)–C(103)	1.201(11)
O(2)–C(104)	1.209(10)
C(101)–C(102)	1.378(11)
C(101)–C(104)	1.481(11)
C(102)–C(103)	1.468(11)
C(103)–C(104)	1.554(12)
S(1)–Pd–S(2)	92.9(1)
S(1)–Pd–S(2')	87.1(1)
Pd–S(1)–C(101)	97.4(3)
Pd–S(2)–C(102)	97.9(3)
C(104)–C(101)–C(102)	92.2(6)
C(101)–C(102)–C(103)	94.6(6)
C(102)–C(103)–C(104)	86.0(6)
C(103)–C(104)–C(101)	87.1(6)

[a] e.s.d.s given in parentheses.

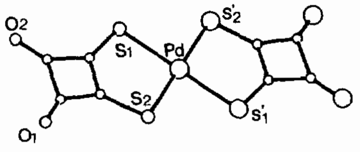

Fig. 1. ORTEP view of the $[Pd(dtsq)_2]^{2-}$ anion.

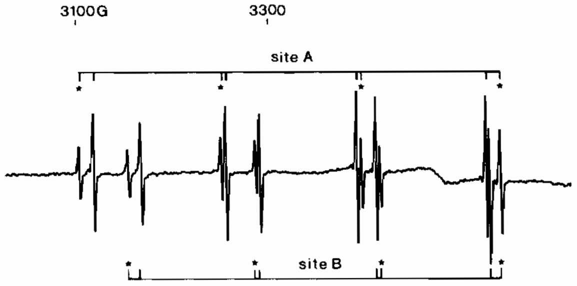

Fig. 2. ESR spectrum obtained at room temperature with a single crystal of $[Pd(dtsq)_2](PPh_4)_2$ doped with $[Cu(dtsq)_2](PPh_4)_2$. The signals marked with a star correspond to ^{65}Cu (klystron frequency: 9.745 GHz).

Electron Spin Resonance

The angular variation of the ESR signals obtained with a single crystal of $[Pd(dtsq)_2](Ph_4P)_2$ doped with the copper(II) complex has been obtained by rotating the crystal around the three orthogonal axes of an *XYZ* referential whose orientation with respect to the crystallographic axes is given by: OZ perpendicular to the plane 101, −OY parallel to the *b* axis, and (OX, c*) angle = 40°. An example of an ESR spectrum is shown in Fig. 2. The contributions of both isotopes ^{63}Cu and ^{65}Cu are clearly observed. The angular dependence of the ESR lines associated with the ^{63}Cu isotope are given in Fig. 3. In accordance with the crystal symmetry (monoclinic) two sets of curves are obtained in the planes OXY and OYZ. The fact that the two sets of lines do not perfectly coalesce in the OXZ plane is due to a slight misalignment of OY which does not perfectly coincide with the *b* axis. For some orientations the forbidden transitions ($\Delta M_I = \pm 1, \pm 2$) are clearly detected; we have attempted to use their position and intensity in order to determine the quadrupolar coupling. However it appears that this interaction is weak and practically does not affect the ESR lines. This implies a maximum value for the quadrupolar interaction which is less than 5 MHz. Finally, the angular variations lead to the *g* and magnetic hyperfine tensors shown in Table III.

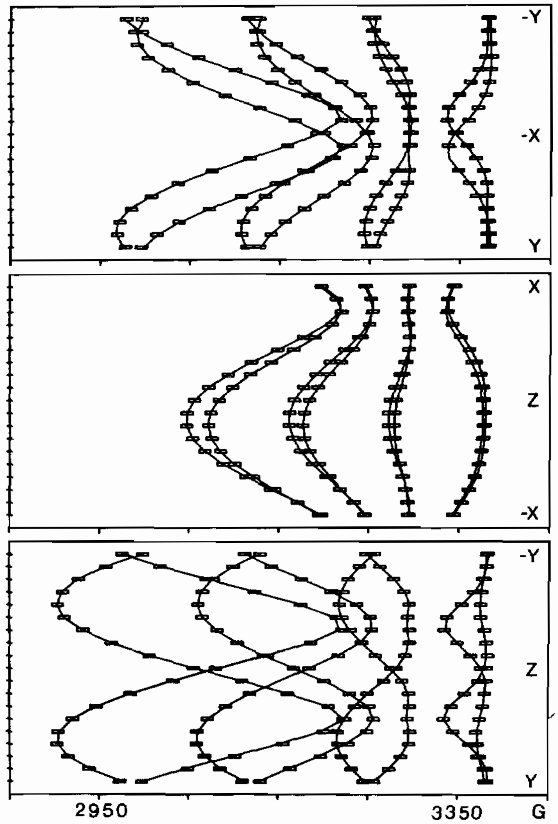

Fig. 3. Angular variation of the ESR signals obtained with a single crystal of $[Pd(dtsq)_2](PPh_4)_2$ doped with $[Cu(dtsq)_2](PPh_4)_2$. The rectangles correspond to the experimental line positions (^{63}Cu), the solid lines have been calculated by using the tensors given in Table III.

TABLE III. *g* and ^{63}Cu Hyperfine Tensors for $[(dtsq)_2Cu(II)](PPh_4)_2$ Trapped in a Single Crystal of $[(dtsq)_2Pd](Ph_4P)_2$[a]

Eigenvalues	Eigenvectors		
	X	*Y*	*Z*
g tensor			
2.023	0.444	−0.427	0.787
2.025	0.876	0.390	−0.282
2.119	−0.187	0.815	0.548
^{63}Cu hyperfine tensor			
(−) 107 MHz	−0.162	−0.571	0.804
(−) 110 MHz	0.969	0.058	0.237
(−) 471 MHz	−0.182	0.818	0.544

[a] The eigenvectors for the second site are obtained by reflection in a plane which almost coincides with the *XZ* plane.

An example of an ESR spectrum obtained with a single crystal of $[Cu(dtsq)_2](Ph_4P)_2$ is shown in Fig. 4. As previously noted [7], the linewidth is large and reflects the magnetic interaction with the environment. The copper hyperfine structure is nevertheless clearly observed and it is possible to follow the angular dependence of these lines. Although the linewidth prevents an accurate measure of the line positions, we could verify that the tensors found with

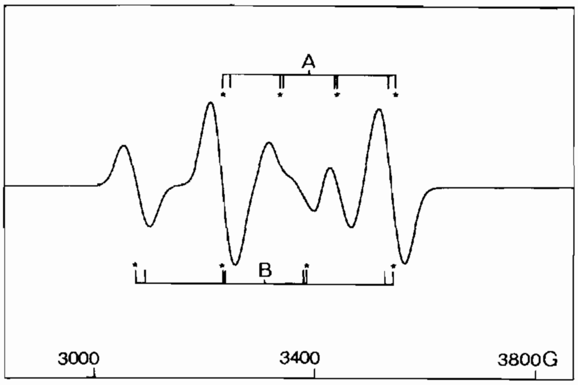

Fig. 4. Typical ESR spectrum obtained with a single crystal of $[Cu(dtsq)_2](PPh_4)_2$. (A and B correspond to two sites which are magnetically distinct.)

the doped $[Pd(dtsq)_2](Ph_4P)_2$ crystal allowed us to generate the experimental curves obtained with the pure crystal of $[Cu(dtsq)_2](Ph_4P)_2$.

Discussion

Both the g factor and the ^{63}Cu hyperfine coupling obtained with a doped single crystal of $[Pd(dtsq)_2](Ph_4P)_2$ are characteristic of a Cu(II) ion in a square planar environment: (i) axial symmetry of the tensors ($2.0023 < g_\perp < g_\parallel$, $T_\perp < T_\parallel$); (ii) alignment of the eigenvectors $g_\parallel$ and $T_\parallel$; (iii) orientation of the $g_\parallel$ and $T_\parallel$ eigenvectors along the direction n which is perpendicular to the plane formed by the sulfur atoms [$(\vec{n}, \vec{T}_\parallel)$ angle = 5°]. Furthermore, the small value estimated for the quadrupolar interaction is consistent with previous results obtained with Cu(II) complexes in which the metal ion is coordinated to four sulfur atoms [15]. For such a planar system the SOMO is principally composed of the Cu $d_{x^2-y^2}$ orbital and the sulfur σ-orbitals. The σ-covalency factor α^2 can be estimated from the two following equations [16] which relate the ^{63}Cu magnetic hyperfine coupling to the g tensor and the Fermi contact parameter K

$$T_\parallel = -K + P_o[(-4/7)\alpha^2 + (g_\parallel - g_e) + 3(g_\perp - g_e)/7]$$

$$T_\perp = -K + P_o[(2/7)\alpha^2 + 11(g_\perp - g_e)/14]$$

The constant P_o (magnetic dipole–dipole coupling between the unpaired electron and ^{63}Cu) is equal to 389 cm^{-1} [17]. α^2 is found to be equal to 0.48 and is quite similar with the values reported for other Cu(II) complexes in which the metal is coordinated to four sulfur atoms: $Cu(mnt)^{2-}$, $\alpha^2 = 0.45$ [16]; $Cu(Et_2NCS_2)_2$, $\alpha^2 = 0.47$ [18]. As previously mentioned [16] this covalency factor is considerably less than that measured with CuO_4 complexes (for $Cu(acac)_2$, $\alpha^2 = 0.71$) and may be correlated with a higher capability of the sulfur ligand to give rise to π-bonding back donation.

TABLE IV. Conductivity (Ω^{-1} cm^{-1}) and Metal–Metal Distances (Å) for some Dithiosquarato Complexes

Compound		Conductivity (Ω^{-1} cm^{-1})	Metal–Metal distance (Å)
$[Pd(dtsq)_2]X_2$	X = K	2×10^{-5}	6.29
	$X = Ph_4P$	7×10^{-8}	11.04
$[Cu(dtsq)_2]X_2$	X = K	reductive process occurs	
	$X = Ph_4P$	1×10^{-9}	11.02
$[Ni(dtsq)_2]X_2$	X = K	1×10^{-5}	6.4
	$X = Ph_4P$	5×10^{-9}	

The ESR spectra obtained with a crystal of pure $[Cu(dtsq)_2](Ph_4P)_2$ are not strongly affected by the paramagnetic surrounding: the linewidth is appreciably increased but the Cu hyperfine structure is clearly observed and is consistent with the results obtained with the isolated complex. The various intermetallic interactions (exchange and dipolar interactions) remain therefore very weak. This lack of interaction is obviously due to the large distance between the metal ions and is also reflected by the small conductivity measured on these two compounds (Table IV). This insulator behaviour contrasts with the rather high conductivity measured with the $[M(dtsq)_2]K_2$ (M = Pd, Ni) complexes and it is worthwhile comparing the crystal structure of these various compounds.

In each case the structure of the anion remains unchanged: the two ligands and the metal lie in the same plane and the metal sulfur distance remains the same (e.g. 2.33 Å for the palladium complex). The planar anions are stacked along two directions oriented parallel to the shortest crystalline axis: one passes through the origin and the other one passes through the center of the unit cell. The distance between two successive planes in $[Pd(dtsq)_2]K_2$ has been found [6] to be equal to 3.51 Å, interstack interactions are then possible since the O...O and O...S distances (3.5–3.6 Å) are not far removed from the sum of van der Waals radii. So, $[M(dtsq)_2]K_2$ can be viewed as two-dimensional materials which explains their semi-conductor properties. For $[M(dtsq)_2](Ph_4P)_2$ complexes, the bulkiness of the cation enhances the cell dimensions. The metal–metal distances increase (from 6.2 Å for the potassium compound to 11.0 Å for the phosphonium compound) as well as the interstack distance and the interstack interactions are precluded. The green colour observed for the palladium complexes related to the electronic structure of the molecular unit is retained for the potassium as well as for the tetraphenylphosphonium salts, but the metallic luster associated with electronic delocalization over all the framework is only observed for the potassium salts.

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