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The Structure of a Dinuclear Silver(I) Complex: $Ag_2[S_2C_2(CN)_2][P(C_6H_5)_3]_4$

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Abstract

The crystal structure of the dimeric Ag maleonitriledithiolate complex, $Ag_2[S_2C_2(CN)_2][P(C_6H_5)_3]_4$ (**1**), has been performed. Complex **1** crystallizes in the space group $P2_1/c$ with $a = 12.2898(77)$, $b = 23.8325(91)$, $c = 23.1790(118)$ Å, $\beta = 101.315(43)°$ and $Z = 4$. Refinement using 3253 reflections with $F_o^2 > 3\sigma(F_o^2)$ yielded $R = 0.0662$, $R_w = 0.0669$. The most interesting aspect of the structure is the strong bridging interaction of the chelating maleonitriledithiolate ligand with the second Ag center, where a Ag–S distance of 2.478 Å is observed. The residual bonding capability of the sulfur atoms in the chelating anion $[Ag(S_2C_2(CN)_2)(PPh_3)_2]^-$ for $[Ag(PPh_3)_2]^+$ is demonstrated.

Introduction

Transition metal maleonitriledithiolate complexes have been extensively studied [1, 2]. These complexes are noted for their stability and their redox chemistry. The maleonitriledithiolate (MNT) ligand uses the chelating mode when coordinating to a metal center [1]. The polymeric silver–MNT complex, $[Ag_2(MNT)]_x$, reacts with triphenylphosphine to produce complexes having the formulation $Ag_2(MNT)(PPh_3)_4$ (**1**) [3]. Complex **1** demonstrates remarkable conductivity in acetone solution resulting from what is thought to be dissociation into an anion–cation pair [3]. Maleonitriledithiolate complexes are known in which an MNT ligand uses a sulfur atom as both a chelating and bridging center to form dimeric metal complexes in the solid state [1, 2, 4]. Since dissociation occurs in solution to the ionic forms, presumably $[Ag(S_2C_2(CN)_2)(PPh_3)_2]^-$ and $[Ag(PPh_3)_2]^+$, a crystal structure determination was performed on complex **1** to establish its solid state structure.

Experimental

X-ray Data Collection and Reduction

Yellow crystals of the title compound were grown form dichloromethane layered with hexane. A suitable crystal with dimensions 0.15 × 0.20 × 0.20 mm^3 was mounted on a glass fiber with epoxy. Diffraction experiments were performed on a Nicolet P3F four-cycle diffractometer controlled by a Data General Nova 4 mini-computer using Mo Kα radiation. The initial orientation matrix was obtained from eight machine centered reflections selected from a rotation photograph. Nineteen reflections from $25° < 2\theta < 30°$ were used to determine the final lattice parameters and orientation matrix. Data was collected at ambient temperature over the range $2° < 2\theta < 40°$. A total of 8233 reflections were obtained, of which 3253 were considered unique and observed. Three standard reflections were measured every 97 reflections; their intensity showed a 25 percent decomposition over the course of data collection. The data were corrected for decay, absorption, Lorentz and polarization effects. Data reduction was performed using the SHELXTL (version 4.1) crystallographic computational package on a Data General Eclipse S140 mini-computer.

Structure Solution and Refinement

The space group was uniquely determined to be $P2_1/c$ by its systematic absences. The Ag atom positions were determined using the Patterson heavy atom method. The remaining non-hydrogen atoms were determined by successive difference Fourier calculations. All phenyl rings were refined as rigid bodies with fixed C–C distances of 1.395 Å and C–C–C angles of 120°. Hydrogen atoms were fixed to phenyl carbons at a distance of 0.98 Å, with the hydrogens of each ring having a common temperature factor. All non-hydrogen atoms were refined anisotropically. The final refinement yielded $R = 0.0662$ and $R_w = 0.0669$. Crystal data and collection parameters are found in Table I (see also 'Supplementary Material').

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TABLE I. Crystallographic Data for $(Ag_2(MNT)(PPh_3)_4)$

Formula	$Ag_2P_4S_2N_2C_{76}H_{60}$
Formula weight	1405.07
Space group	$P2_1/c$
Systematic absences	$h0l$, $00l$, $l = 2n$; $0k0$, $k = 2n$
a (Å)	12.290(8)
b (Å)	23.832(9)
c (Å)	23.179(12)
α (deg)	90.02(4)
β (deg)	101.32(4)
γ (deg)	90.10(4)
V (Å^3)	6657.07(574)
Z	4
D_c (g/cm^3)	1.40
Crystal size (mm)	0.15 × 0.20 × 0.20
$F(000)$ (e)	2863.68
μ(Mo Kα) (cm^{-1})	7.80
Radiation	monochromated in Mo Kα ($\lambda\alpha$ = 0.71073 Å) incident beam
Orientation reflections, number range (2θ)	19, 25–30
Temperature (°C)	25
Scan method	$2\theta/\theta$
Data collection range, 2θ (deg)	2–40
Total reflections measured	8233
Number unique data, total with $F_o^2 > 3\sigma(F_o^2)$	7696, 3253
Check reflections	3, every 97
Number of parameters refined	643
Transmission factors, max./min.	0.899/0.743
R^a	0.0662
$R_w{}^b$	0.0669
Goodness-of-fit indicator^c	1.660
Largest shift/e.s.d., final cycle	0.003
Largest peak (e/Å^3)	0.89

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma \sqrt{w}(|F_o| - |F_c|)]/\Sigma \sqrt{w}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + 0.001|F_o|^2]$. ^{c}Goodness-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

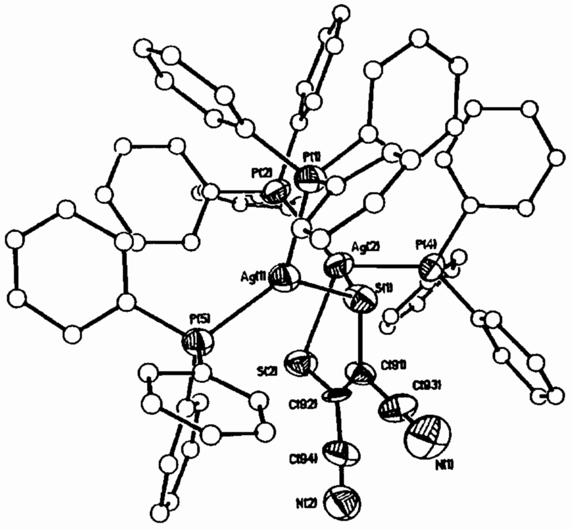

Fig. 1. Molecular structure of $Ag_2[S_2C_2(CN)_2][P(C_6H_5)_3]_4$ and the atom labelling scheme.

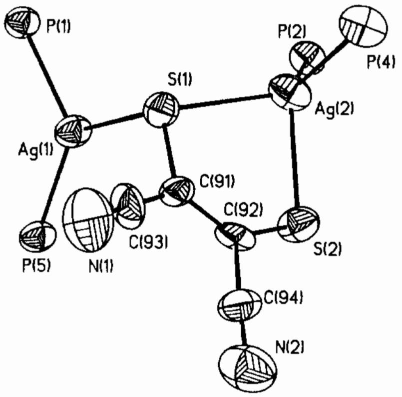

Fig. 2. Central core of 1 showing the bonding coordination around the two Ag centers, and the bridging and chelating nature of the MNT ligand.

Results and Discussion

A thermal ellipsoid drawing of the structure determined for $Ag_2[S_2C_2(CN)_2][P(C_6H_5)_3]_4$ (1) is shown in Figs. 1 and 2. Selected interatomic distances and angles are given in Table III, while the atomic coordinates may be found in Table II. In the title compound, the two metal atoms are bridged by one sulfur atom of the chelating maleonitriledithiolate, MNT, ligand. The two silver atoms are not bonded to each other, having a Ag–Ag separation of 4.392 Å. The geometries around the two Ag metal centers are markedly different. Ag(1) has a planar, three coordinate geometry, while Ag(2) has a slightly distorted tetrahedral ligand arrangement. The distortion of the tetrahedral geometry for Ag(2) results form the tight dithiolate bite angle; in this case there is a S(1)–Ag(2)–S(2) angle of 82.2°. The presence of two bulky triphenylphosphine ligands also contributes to the distortion.

The most significant structural feature in this molecule is the variation in both the chelating and bridging Ag–S distances. The chelating distances for the Ag–MNT are 2.653 Å and 2.568 Å for Ag(2)–S(1) and Ag(2)–S(2) respectively. Such variation in metal–sulfur bond lengths is typically not seen in MNT coordination chemistry. Even in complexes where one sulfur atom acts as a bridging atom for dimeric metal MNT complexes, the variations in metal–sulfur distances are quite small [5, 6]. The shortest Ag–S distance is 2.478 Å and corresponds to the Ag(1)–S(1) bond distance. This is surprising in light of conductivity measurements in acetone solution and ^{31}P NMR results which

TABLE II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for ($Ag_2(MNT)(PPh_3)_4$)

Atom	*x*	*y*	*z*	U_{eq}[a]
Ag(1)	3120(1)	1609(1)	8341(1)	50(1)
Ag(2)	1889(1)	1737(1)	6435(1)	56(1)
P(1)	2268(4)	753(2)	8695(2)	47(2)
C(11)	3660(10)	11(5)	8303(4)	55(8)
C(12)	4377(10)	−447(5)	8338(4)	55(8)
C(13)	4630(10)	−759(5)	8856(4)	66(9)
C(14)	4166(10)	−614(5)	9338(4)	74(9)
C(15)	3450(10)	−157(5)	9303(4)	58(8)
C(16)	3197(10)	155(5)	8785(4)	51(7)
C(21)	942(10)	667(5)	9564(5)	71(9)
C(22)	718(10)	755(5)	10125(5)	75(9)
C(23)	1498(10)	1025(5)	10554(5)	79(10)
C(24)	2502(10)	1206(5)	10423(5)	82(10)
C(25)	2726(10)	1119(5)	9863(5)	68(9)
C(26)	1946(10)	849(5)	9434(5)	49(7)
C(31)	681(11)	−80(5)	8312(5)	59(8)
C(32)	−318(11)	−287(5)	7989(5)	71(9)
C(33)	−1021(11)	65(5)	7605(5)	80(10)
C(34)	−725(11)	624(5)	7543(5)	76(10)
C(35)	274(11)	831(5)	7866(5)	53(8)
C(36)	977(11)	478(5)	8250(5)	50(7)
P(2)	2742(4)	858(2)	6179(2)	52(2)
C(61)	4064(11)	701(5)	5341(7)	68(9)
C(62)	4289(11)	721(5)	4774(7)	94(12)
C(63)	3494(11)	929(5)	4310(7)	112(14)
C(64)	2474(11)	1116(5)	4413(7)	88(11)
C(65)	2249(11)	1095(5)	4980(7)	70(9)
C(66)	3044(11)	888(5)	5444(7)	48(7)
C(71)	1619(10)	−118(5)	5680(4)	59(8)
C(72)	968(10)	−593(5)	5709(4)	82(10)
C(73)	679(10)	−744(5)	6241(4)	81(10)
C(74)	1039(10)	−419(5)	6743(4)	70(9)
C(75)	1690(10)	57(5)	6714(4)	74(10)
C(76)	1979(10)	207(5)	6182(4)	43(7)
C(81)	4464(11)	149(4)	6712(5)	71(9)
C(82)	5478(11)	38(4)	7084(5)	89(11)
C(83)	6083(11)	474(4)	7398(5)	102(12)
C(84)	5674(11)	1021(4)	7340(5)	107(13)
C(85)	4660(11)	1132(4)	6968(5)	79(10)
C(86)	4055(11)	696(4)	6654(5)	58(8)
S(1)	1760(4)	2028(2)	7524(2)	54(2)
S(2)	3103(4)	2622(2)	6509(2)	57(2)
C(92)	2586(13)	2969(5)	7047(7)	42(7)
C(91)	2095(12)	2742(6)	7466(7)	39(7)
C(93)	1584(17)	3119(7)	7830(8)	62(9)
N(1)	1222(16)	3412(8)	8114(8)	107(10)
N(2)	2984(13)	4031(8)	7079(7)	83(8)
C(94)	2771(16)	3555(8)	7080(8)	65(8)
P(4)	−14(4)	2016(2)	5857(2)	56(2)
C(101)	−792(11)	2596(6)	6696(6)	81(10)
C(102)	−1295(11)	3038(6)	6938(6)	95(11)
C(103)	−1659(11)	3509(6)	6598(6)	91(11)
C(104)	−1520(11)	3538(6)	6016(6)	101(12)
C(105)	−1017(11)	3096(6)	5773(6)	58(8)
C(106)	−653(11)	2625(6)	6113(6)	74(9)
C(111)	−743(9)	931(6)	5919(5)	61(8)
C(112)	−1533(9)	508(6)	5903(5)	73(9)
C(113)	−2660(9)	641(6)	5790(5)	85(11)
C(114)	−2996(9)	1198(6)	5694(5)	131(14)
C(115)	−2206(9)	1621(6)	5710(5)	93(10)
C(116)	−1079(9)	1488(6)	5822(5)	58(8)
C(121)	899(10)	2504(5)	4996(6)	60(9)
C(122)	983(10)	2669(5)	4429(6)	86(10)
C(123)	141(10)	2534(5)	3953(6)	81(11)
C(124)	−785(10)	2232(5)	4043(6)	73(10)
C(125)	−869(10)	2066(5)	4609(6)	62(8)
C(126)	−27(10)	2202(5)	5086(6)	56(8)
P(5)	4949(4)	1979(2)	8818(2)	51(2)
C(41)	5811(8)	917(5)	8965(5)	48(7)
C(42)	6646(8)	513(5)	9024(5)	75(9)
C(43)	7728(8)	671(5)	8995(5)	82(10)
C(44)	7975(8)	1232(5)	8907(5)	108(13)
C(45)	7140(8)	1636(5)	8848(5)	73(9)
C(46)	6058(8)	1478(5)	8877(5)	48(7)
C(51)	6042(10)	3028(6)	8859(4)	68(9)
C(52)	6429(10)	3491(6)	8591(4)	80(10)
C(53)	6234(10)	3529(6)	7979(4)	91(11)
C(54)	5652(10)	3103(6)	7635(4)	89(10)
C(55)	5265(10)	2640(6)	7903(4)	82(10)
C(56)	5460(10)	2602(6)	8516(4)	54(8)
C(131)	5865(9)	2044(4)	10031(6)	58(8)
C(132)	5890(9)	2250(4)	10597(6)	69(9)
C(133)	5040(9)	2596(4)	10707(6)	85(11)
C(134)	4165(9)	2738(4)	10250(6)	79(10)
C(135)	4139(9)	2532(4)	9684(6)	75(10)
C(136)	4989(9)	2185(4)	9575(6)	44(7)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised $\mathbf{U}_{ij}$ tensor.

indicate an ionic equilibrium at room temperature (eqn. (1)) that would require the breaking of this Ag(1)–S(1) bond [3]. This short bond distance to a second metal center is also contrary to typical dimeric systems where the longest metal–sulfur interaction is the bridging attachment. The strong interaction of the sulfur atom that takes part in bridging to the second metal center influences the bonding distances related to the chelating MNT. This causes the asymmetry in bond lengths observed for complex **1**.

$$Ag_2(MNT)(PPh_3)_4 \rightleftharpoons [Ag(MNT)(PPh_3)_2]^- + [Ag(PPh_3)_2]^+ \tag{1}$$

Within the MNT ligand itself, the bond distances are not altered significantly by the strong interaction of S(1) to the second metal center. The average S–C bond length of 1.739 Å indicates some partial double bond character. The C–C distance of 1.352 Å for the carbons of the chelate ring is not significantly different from the average C–CN distance of 1.436 Å. Carbon–carbon bond lengths of this type are typical for partial double bonds. It is also consistent with

TABLE III. Bond Lengths (Å) and Bond Angles (deg) for $(Ag_2(MNT)(PPh_3)_4)$

Bond lengths			
Ag(1)–P(1)	2.504(7)	N(2)–C(94)	1.164(27)
Ag(1)–P(5)	2.463(7)	P(4)–C(116)	1.804(14)
Ag(2)–S(1)	2.653(7)	P(5)–C(46)	1.798(12)
Ag(2)–P(4)	2.546(7)	P(5)–C(136)	1.812(15)
Ag(1)–S(1)	2.478(7)	P(1)–C(26)	1.845(14)
Ag(2)–P(2)	2.468(7)	P(2)–C(66)	1.816(17)
Ag(2)–S(2)	2.568(7)	P(2)–C(86)	1.808(14)
P(1)–C(16)	1.813(13)	S(2)–C(92)	1.719(17)
P(1)–C(36)	1.834(13)	C(92)–C(94)	1.414(24)
P(2)–C(76)	1.812(14)	C(93)–N(1)	1.110(28)
S(1)–C(91)	1.761(16)	P(4)–C(106)	1.807(15)
C(92)–C(91)	1.353(24)	P(4)–C(126)	1.838(16)
C(91)–C(93)	1.456(26)	P(5)–C(56)	1.807(14)
Bond angles			
P(1)–Ag(1)–S(1)	108.5(2)	P(1)–Ag(1)–P(5)	123.1(2)
S(1)–Ag(1)–P(5)	128.2(2)	P(2)–Ag(2)–S(1)	123.9(2)
P(2)–Ag(2)–S(2)	116.4(2)	S(1)–Ag(2)–S(2)	82.2(2)
P(2)–Ag(2)–P(4)	119.1(2)	S(1)–Ag(2)–P(4)	102.3(2)
S(2)–Ag(2)–P(4)	106.4(2)	Ag(1)–P(1)–C(16)	112.6(5)
Ag(1)–P(1)–C(26)	112.5(4)	C(16)–P(1)–C(26)	103.6(5)
Ag(1)–P(1)–C(36)	118.4(4)	C(16)–P(1)–C(36)	104.0(6)
C(26)–P(1)–C(36)	104.3(6)	Ag(2)–P(2)–C(66)	111.5(4)
Ag(2)–P(2)–C(76)	118.8(5)	C(66)–P(2)–C(76)	103.8(6)
Ag(2)–P(2)–C(86)	114.0(4)	C(66)–P(2)–C(86)	104.9(7)
C(76)–P(2)–C(86)	102.4(6)	Ag(1)–S(1)–Ag(2)	117.7(2)
Ag(1)–S(1)–C(91)	108.5(5)	Ag(2)–S(1)–C(91)	97.0(6)
Ag(2)–S(2)–C(92)	98.7(5)	S(2)–C(92)–C(91)	127.5(11)
S(2)–C(92)–C(94)	115.8(13)	C(91)–C(92)–C(94)	116.4(15)
S(1)–C(91)–C(92)	125.8(12)	S(1)–C(91)–C(93)	114.7(13)
C(92)–C(91)–C(93)	118.3(14)	C(91)–C(93)–N(1)	178.1(22)
C(92)–C(94)–N(2)	174.6(22)	Ag(2)–P(4)–C(106)	116.8(5)
Ag(2)–P(4)–C(116)	115.1(4)	C(106)–P(4)–C(116)	102.5(7)
Ag(2)–P(4)–C(126)	114.0(5)	C(106)–P(4)–C(126)	101.8(7)
C(116)–P(4)–C(126)	105.0(6)	Ag(1)–P(5)–C(46)	114.1(4)
Ag(1)–P(5)–C(56)	118.3(4)	C(46)–P(5)–C(56)	105.0(6)
Ag(1)–P(5)–C(136)	112.3(4)	C(46)–P(5)–C(136)	103.3(5)
C(56)–P(5)–C(136)	102.0(5)		

delocalization of electrons throughout the pi orbitals of the MNT ligand. The bond lengths for the MNT are all within normal observed distances for other metal dithiolate complexes.

The average Ag–P bond length is 2.495 Å. All phosphorus atoms are tetrahedral, having average P–C bond lengths of 1.816 Å.

In the solid state, complex **1** can best be viewed as containing two Ag atoms in the +1 oxidation state. This is consistent with the short Ag(1)–S(1) bond length and with the coordination geometry of the MNT ligand. This is also consistent with the ^{31}P NMR results, in which it has been shown that dissociation occurs to give $[Ag(S_2C_2(CN)_2)(P(Ph_3)_2]^-$ and $[Ag(PPh_3)_2]^+$ [3].

Supplementary Material

Tables of anisotropic temperature factors, hydrogen coordinates, and observed and calculated structure factors have been deposited with the Editor-in-Chief.

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