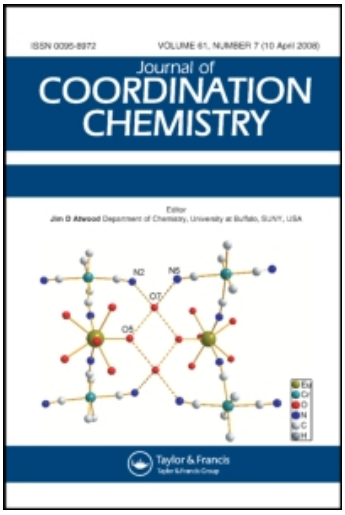

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SYNTHESES AND CRYSTAL STRUCTURES OF ISOMALONONITRILE DITHIOLATO COMPLEXES $(Bu_4N)_2Zn(i\text{-mnt})_2$ AND $(Et_4N)_2Pd(i\text{-mnt})_2$

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SYNTHESES AND CRYSTAL STRUCTURES OF ISOMALONONITRILE DITHIOLATO COMPLEXES $(Bu_4N)_2Zn(i\text{-mnt})_2$ AND $(Et_4N)_2Pd(i\text{-mnt})_2$

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Two isomalononitrile dithiolato complexes, $(Bu_4N)_2Zn(i\text{-mnt})_2$ *(1)* and $(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)* were synthesized and characterized by elemental analysis, IR and electronic spectroscopy. Their structures have been crystallographically determined. The reaction of $(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)* with $(Et_4N)_2WS_4$ gives $(Et_4N)_2WS_4Pd(i\text{-mnt})$.

KEYWORDS: synthesis, X-ray structure, isomalononitrile dithiolate, zinc, palladium

INTRODUCTION

Different structures of isomalononitrile dithiolato (*i*-mnt) metal complexes and cluster compounds have been found during the past two decades. Among them are the mononuclear complexes, $M(i\text{-mnt})_2^{2-}$ [M = Pt(II),[1] Cd(II),[2] Pb(II)[3]], binuclear complexes such as $Au_2(PPh_3)_2(i\text{-mnt})$,[4] $\{Au(i\text{-mnt})Cl\}_2^{5-}$,[6] $Mo_2O_2S_2(i\text{-mnt})_2^{2-}$,[7] the trunuclear complex $[Ag(P(C_6H_5)_3)_2]_2Ni(i\text{-mnt})_2$,[8] and clusters containing the cores $Ag_6(i\text{-mnt})_6^{6-}$,[9] $Cu_8(i\text{-mnt})_6^{4-}$.[10]

Recently our research concentrated on the syntheses and nonlinear optical properties of mixed metal cluster compounds.[11–13] In an attempt to synthesize Zn(Pd)-Mo(W)-S clusters we used 1,1-dithiolato ligands such as isomalononitrile dithiolate (*i*-mnt) and obtained two complexes, $(Bu_4N)_2Zn(i\text{-mnt})_2$ *(1)* and $(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)*. There have been some reports of Zn and Pd complexes with isomalononitrile dithiolate,[14–18] but structures have not appeared until now. In this

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paper we report the syntheses and crystal structures of the title compounds, together with the reaction of $(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)* and $(Et_4N)_2WS_4$.

EXPERIMENTAL

Chemicals

Sodium isomalononitrile dithiolate $Na_2(i\text{-mnt})$[19] and $(Et_4N)_2WS_4$[20] were prepared as described in the literature. $ZnCl_2$ and $PdCl_2$ were of A.R. grade. Other materials were used as received without further purification.

Physical measurements

IR spectra in the 4000–400 cm^{-1} range were obtained on a Nicolet 170sx FT-IR spectrophotometer in KBr pellets. Electronic spectra in CH_2Cl_2 solutions were recorded on a Shimadzu spectrophotometer. Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer 240c elemental analyser. Zinc and Palladium analyses were carried out using a Jarrell-Ash 1100 + 2000 ICP spectrometer.

Syntheses of the complexes

$(Bu_4N)_2Zn(i\text{-mnt})_2$ *(1)*

Addition of $Na_2(i\text{-mnt})$ (20 mmol) in 10 cm^3 of H_2O to a solution of $ZnCl_2$ (10 mmol) and Bu_4NBr (40 mmol) in 50 cm^3 of H_2O immediately produced a white syrupy precipitate. After stirring for a while, the precipitate solidified. The product was recrystallized from methanol-water (2:1) and pale yellow crystals were obtained. Found: C, 57.55; H, 8.47; N, 9.95; Zn, 8.10%. $C_{40}H_{72}N_6S_4Zn$ (calcd): C, 57.94; H, 8.76; N, 10.14; Zn, 7.72%. IR 2196 cm^{-1} ($\nu C{\equiv}N$).

$(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)*

$PdCl_2$ (5 mmol) and Et_4NCl (10 mmol) were heated in 50 cm^3 of methanol to dissolve. To the solution was added solid $Na_2(i\text{-mnt})$ (10 mmol). After stirring for one hour the orange-red solution was filtered. $(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)* crystallized as orange-red prisms while the solution evaporated slowly in air. Found: C, 44.20; H, 6.00; N, 12.70; Pd, 16.02%. $C_{24}H_{40}N_6PdS_4$ (calcd): C, 44.57; H, 6.24; N, 13.00; Pd, 16.39%. IR 2199 cm^{-1} ($\nu C{\equiv}N$).

Reaction of (2) with $(Et_4N)_2WS_4$

Solid $(Et_4N)_2WS_4$ (0.5 mmol) was added to a solution of 0.5 mmol *(2)* in 10 cm^3 of CH_2Cl_2. The mixture was stirred for one hour and filtered. The filtrate was layered with 10 cm^3 of CH_3OH and left open to the air for several days, when yellow crystals formed. Found: C, 29.56; H, 5.04; N, 6.64; Pd, 12.70%. $C_{20}H_{40}N_4PdS_6W$ (calcd): C, 29.32; H, 4.92; N, 6.84; Pd, 12.99%.

X-ray data collection and structure determination

A crystal was scanned on a R3M/E diffractometer using graphite-monochromated Mo-Kα radiation. Lattice parameters and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 25 automatically centred reflections. Crystal data and conditions of data collection are given in Table 1. Intensities were corrected for Lp effects while absorption correction were not made to the diffraction data.

The structure of *(1)* was solved using direct methods. Zn and some S atoms were first obtained. The other non-H atoms were deduced from successive Fourier syntheses. The structure of *(2)* was solved by the Patterson method. The position of the Pd atom was obtained from analysis of Patterson functions; the remaining non-H atoms were located from successive Fourier syntheses. The refinement of both structures was performed by full-matrix least-squares techniques. Atomic coordinates and anisotropic displacements of all non-H atoms were refined. The positions of H atoms were calculated geometrically for *(1)* and located from successive difference-Fourier syntheses and refined isotropically for *(2)*. All computations were performed on an Eclipse S140 computer using the SHELXTL(1985) program package. Fractional coordinates and equivalent temperature factors, important bond lengths and angles are given in Tables 2 and 4 for *(1)*, and Tables 3 and 5 for *(2)*.

Table 1 Crystallographic data for $(Bu_4N)_2Zn(i\text{-mnt})_2$ *(1)* and $(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)*.

Chemical formula	$ZnS_4N_6C_{40}H_{72}$	$PdS_4N_6C_{24}H_{40}$
Formula weight	830.9	647.04
Colour	Pale yellow	Orange-red
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	$P2_1/c$
Unit cell parameters		
a (Å)	51.254(8)	9.511(1)
b (Å)	9.281(2)	11.612(2)
c (Å)	30.259(4)	14.820(3)
β (°)	91.63(1)	94.38(1)
V (Å^3)	14388(4)	1631.9(5)
Z	12	2
μ (cm^{-1})	7.40	8.30
F(000)	5616	672
2θ(°)	2–45	2–48
h, k, l ranges	0–56, 0–10, −33–33	0–11, 0–14, −17–17
d_{calc} (g/cm^3)	1.22	1.32
Temperature (*K*)	294	294
Diffractometer	R3M/E	R3M/E
Radiation (Å)	Mo*K*α (0.71073)	Mo*K*α (0.71073)
Solution method	direct methods	Patterson synthesis
Absorption correction	Lp	Lp
Residuals: *R*; R_w	0.0484, 0.0443	0.0324; 0.0298
Goodness of fit	0.904	0.918
No. of unique data	3945	2902
No. obs. with $I>n\sigma(I)$	3945 (n = 2.5)	2045 (n = 1.5)
No. of variables	691	241
Max. shift in final cycle	0.156	−0.185
Largest peaks in final diff. map	0.361, −0.308	0.259, −0.206

Table 2 Positional parameters ($\times 10^4$) and equivalent temperature factors ($Å^2 \times 10^3$) for $(Bu_4N)_2Zn(i\text{-mnt})_2$ *(1)*.

	x/a	*y/b*	*z/c*	U_{eq}
Zn(1)	0	2552(2)	2500	85(1)
Zn(2)	1682(1)	6551(1)	4152(1)	74(1)
S(1)	-153(1)	3548(3)	3155(1)	78(1)
S(2)	272(1)	1442(3)	3039(1)	82(1)
S(3)	1845(1)	7972(3)	3586(1)	87(1)
S(4)	1391(1)	6018(2)	3555(1)	75(1)
S(5)	1533(1)	7276(2)	4846(1)	74(1)
S(6)	1948(1)	5202(2)	4642(1)	77(1)
N(1)	-207(1)	3492(8)	4370(2)	101(3)
N(2)	482(1)	855(8)	4210(2)	110(3)
N(3)	1781(1)	9713(7)	2471(2)	93(3)
N(4)	1088(1)	7100(7)	2461(2)	97(3)
N(5)	1539(1)	7077(8)	6062(2)	111(3)
N(6)	2186(1)	4250(8)	5783(2)	124(4)
N(7)	615(1)	6172(6)	4375(2)	66(2)
N(8)	1052(1)	2392(6)	2230(2)	52(2)
N(9)	2286(1)	9996(6)	1136(2)	61(2)
C(1)	76(1)	2400(8)	3394(2)	66(3)
C(2)	101(1)	2247(7)	3846(2)	60(3)
C(3)	-72(1)	2950(8)	4136(2)	73(3)
C(4)	311(1)	1452(9)	4042(2)	78(3)
C(5)	1576(1)	7329(8)	3300(2)	63(3)
C(6)	1507(1)	7846(7)	2885(2)	59(3)
C(7)	1633(1)	8882(8)	2662(2)	71(3)
C(8)	1273(1)	7425(8)	2657(2)	72(3)
C(9)	1768(1)	6080(7)	5030(2)	60(3)
C(10)	1817(1)	5831(8)	5479(2)	67(3)
C(11)	1657(1)	6515(8)	5794(2)	80(3)
C(12)	2021(1)	4945(9)	5641(2)	80(3)
C(13)	713(1)	4780(8)	4573(2)	76(3)
C(14)	995(2)	4414(8)	4501(2)	82(3)
C(15)	1066(2)	3017(8)	4734(3)	106(4)
C(16)	1346(2)	2615(10)	4715(3)	132(5)
C(17)	765(1)	7447(8)	4550(2)	67(3)
C(18)	787(1)	7615(8)	5044(2)	73(3)
C(19)	897(2)	9113(8)	5155(3)	88(4)
C(20)	930(2)	9344(10)	5641(3)	123(5)
C(21)	328(1)	6242(9)	4501(2)	77(3)
C(22)	185(1)	7615(10)	4406(3)	96(4)
C(23)	-100(1)	7457(10)	4537(3)	119(4)
C(24)	-247(2)	8792(12)	4518(4)	155(6)
C(25)	642(2)	6284(11)	3874(3)	104(4)
C(26)	503(2)	5245(12)	3600(3)	131(5)
C(27)	546(2)	5545(12)	3108(3)	111(5)
C(28)	397(3)	6726(13)	2901(4)	181(7)
C(29)	1001(1)	2383(7)	2723(2)	58(3)
C(30)	1115(1)	1155(8)	2993(2)	67(3)
C(31)	1053(1)	1322(9)	3476(2)	76(3)
C(32)	1145(2)	84(9)	3757(2)	99(4)
C(33)	967(1)	981(7)	2013(2)	58(3)
C(34)	679(1)	592(7)	2053(2)	71(3)
C(35)	615(2)	-784(8)	1808(3)	82(4)
C(36)	330(2)	-1179(9)	1822(3)	106(4)
C(37)	897(1)	3659(7)	2045(2)	57(3)
C(38)	910(1)	3887(7)	1551(2)	64(3)

Table 2 — (Continued)

	x/a	*y/b*	*z/c*	U_{eq}
C(39)	790(1)	5326(8)	1427(2)	70(3)
C(40)	791(2)	5611(9)	935(2)	97(4)
C(41)	1341(1)	2524(7)	2147(2)	56(3)
C(42)	1470(1)	3901(8)	2308(2)	69(3)
C(43)	1759(1)	3907(9)	2203(3)	79(3)
C(44)	1890(1)	5269(10)	2336(3)	121(5)
C(45)	2398(1)	11472(7)	1240(2)	67(3)
C(46)	2433(1)	11842(9)	1727(2)	79(3)
C(47)	2488(1)	13414(9)	1789(2)	82(3)
C(48)	2565(2)	13778(10)	2259(3)	118(4)
C(49)	2430(1)	8807(7)	1388(2)	64(3)
C(50)	2722(1)	8726(8)	1320(2)	71(3)
C(51)	2844(1)	7504(9)	1580(3)	86(3)
C(52)	3132(2)	7375(10)	1508(3)	112(4)
C(53)	2003(1)	10007(9)	1272(2)	76(3)
C(54)	1849(2)	8677(11)	1170(3)	104(4)
C(55)	1568(2)	8857(12)	1305(3)	116(5)
C(56)	1405(2)	7566(13)	1233(4)	161(6)
C(57)	2307(1)	9684(9)	650(2)	78(3)
C(58)	2156(2)	10716(11)	344(2)	114(4)
C(59)	2226(2)	10510(14)	-160(4)	159(7)
C(60)	2110(3)	9169(17)	-292(5)	242(11)

$U_{eq} = (1/3)\Sigma_i\Sigma_j Uij a_i^* a_j^* a_i.a_j$.

Table 3 Positional parameters ($\times 10^4$) and equivalent temperature factors ($Å^2 \times 10^3$) for $(Et_4N)_2Pd(i\text{-}mnt)_2$ *(2)*.

	x/a	*y/b*	*z/c*	U_{eq}
Pd	5000	0	5000	54(1)
S(1)	5426(1)	-70(1)	3478(1)	62(1)
S(2)	6960(1)	1169(1)	4878(1)	66(1)
N(1)	7160(5)	878(4)	1428(2)	119(2)
N(2)	9551(3)	2829(3)	3550(2)	83(1)
N(3)	7739(3)	6381(2)	3970(2)	59(1)
C(1)	6782(3)	889(3)	3732(2)	55(1)
C(2)	7595(3)	1377(3)	3105(2)	58(1)
C(3)	7355(4)	1098(4)	2174(2)	76(1)
C(4)	8676(4)	2181(3)	3354(2)	63(1)
C(5)	7814(4)	5159(3)	4326(2)	69(1)
C(6)	6512(5)	4455(4)	4120(3)	85(2)
C(7)	7339(5)	6391(3)	2960(3)	78(1)
C(8)	8256(6)	5668(5)	2405(3)	94(2)
C(9)	9180(4)	6936(4)	4173(3)	83(2)
C(10)	9278(6)	8183(5)	3904(5)	111(2)
C(11)	6614(4)	7049(3)	4432(3)	80(1)
C(12)	6837(5)	7147(4)	5438(3)	98(2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j Uij a_i^* a_j^* a_i.a_j$.

RESULTS AND DISCUSSION

Electronic spectra

$(Bu_4N)_2Zn(i\text{-mnt})_2$ *(1)* exhibits a UV absorption at $\lambda_{max} = 342$ nm in CH_2Cl_2. The band can be assigned to intraligand $\pi \rightarrow \pi^*$ transitions. $(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)* has two prime UV absorptions in CH_2Cl_2 at $\lambda_{max} = 378$ and 318 nm. The former can be attributed to $d\pi(Pd) \rightarrow \pi^*(i\text{-mnt})$ (metal-to-ligand charge-transfer) and the latter can be assigned to intraligand $\pi \rightarrow \pi^*$ transitions.

Description of the structure of $(Bu_4N)_2Zn(i\text{-}mnt)_2$ (1)

Crystals of *(1)* possess crystallographically-imposed two-fold symmetry (space group C2/c), and consists of twelve $Zn(i\text{-mnt})_2^{2-}$ anions and twenty four tetrabutylammonium cations in the unit cell. The twelve $Zn(i\text{-mnt})_2^{2-}$ anions can be divided into four groups, each of which contains three complex anions: one is located in a special position so that the Zn1 atom sits on a two-fold axis, while the other two anions are on symmetrical positions about the two-fold axis (see Figure 2). The packing diagram (Figure 1) shows that the anions exist discretely and are arranged in a line. The complex anion consists of one Zn atom and two *i*-mnt ligands which act as bidentates. The Zn atom is surrounded by four S atoms coordinated in a tetrahedron. The dihedral angle for Zn1 (Plane 1 and its symmetry equivalent Plane 2 shown in Table 6) is 97.0°, and that for Zn2 (Plane 3 and 4) is 99.3°. That is to

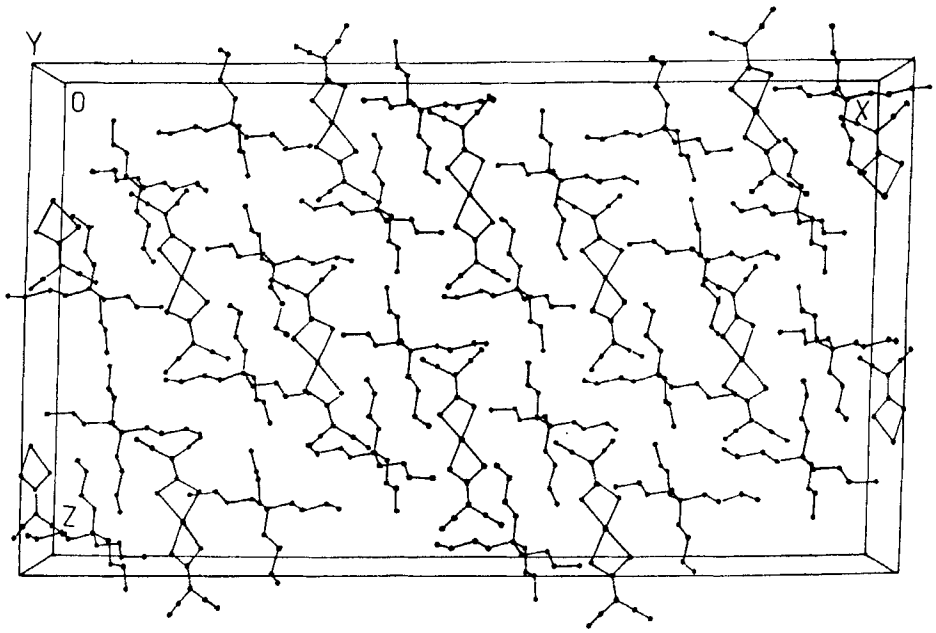


Figure 1 Packing diagram showing the linear arrangement of cations in *(1)*.

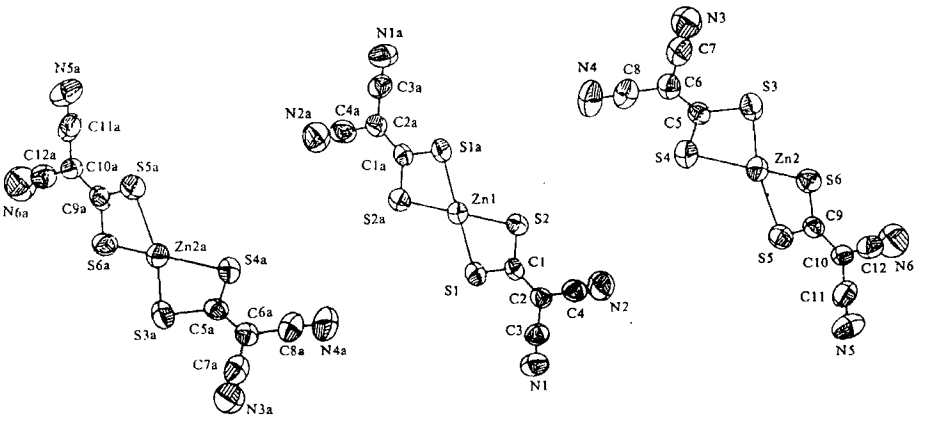


Figure 2 ORTEP drawing of the molecular structure and labelling scheme for the anions in *(1)*. Cations are omitted for clarity.

say that the coordination of Zn2 deviates from the tetrahedron more than that of Zn1.

Zn-S distances range from 2.341 to 2.362Å, which are comparable to 2.347Å found in the polymeric structure of Zn(*O,O'*-diethylphosphoradithiolate)$_2$[22] and are longer than 2.286Å found in $Zn_4(SC_6H_5)_{10}^{2-}$.[23]

Description of the structure of $(Et_4N)_2Pd(i\text{-}mnt)_2$ (2)

Crystals of (2) have crystallographically-imposed symmetrical centres (space group $P2_1/c$), with two $Pd(i\text{-}mnt)_2^{2-}$ anions and four Et_4N^+ cations in a unit cell.

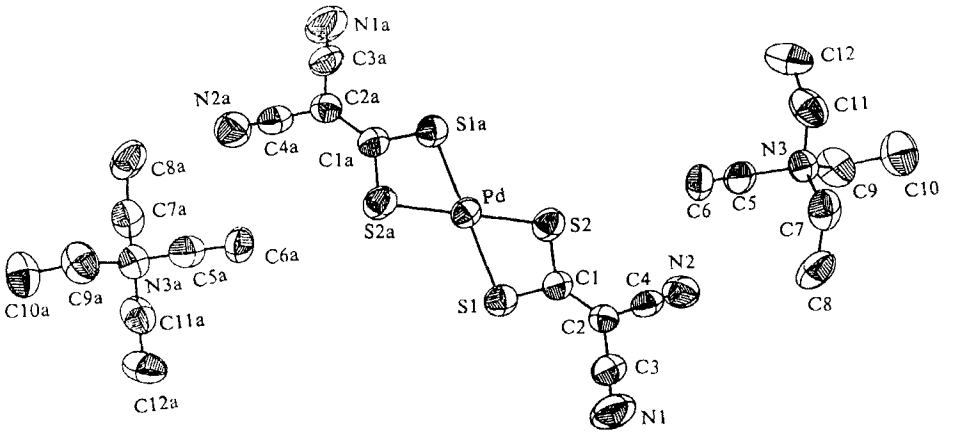


Figure 3 ORTEP drawing of the molecular structure and labelling scheme for *(2)*.

Table 4 Selected bond lengths and angles for $(Bu_4N)_2Zn(i\text{-mnt})_2$ *(1)* (Å and degrees).

Zn(1)-S(1)	2.341(2)	Zn(1)-S(2)	2.351(2)
Zn(2)-S(3)	2.334(2)	Zn(2)-S(4)	2.362(2)
Zn(2)-S(5)	2.352(2)	Zn(2)-S(4)	2.344(2)
S(1)-C(1)	1.728(7)	S(2)-C(1)	1.737(7)
S(3)-C(5)	1.714(6)	S(4)-C(5)	1.738(7)
S(5)-C(9)	1.718(7)	S(6)-C(9)	1.718(7)
N(1)-C(3)	1.125(9)	N(2)-C(4)	1.144(10)
N(3)-C(7)	1.145(10)	N(4)-C(8)	1.147(9)
N(5)-C(11)	1.148(10)	N(6)-C(12)	1.142(11)
C(1)-C(2)	1.376(9)	C(2)-C(3)	1.422(10)
C(2)-C(4)	1.422(10)	C(5)-C(6)	1.381(9)
C(6)-C(7)	1.432(10)	C(6)-C(8)	1.420(9)
C(9)-C(10)	1.395(10)	C(10)-C(11)	1.426(10)
C(10)-C(12)	1.404(11)		
S(1)-Zn(1)-S(2)	78.0(1)	S(1)-Zn(1)-S(1a)	133.5(1)
S(2)-Zn(1)-S(2a)	128.0(1)	S(1)-Zn(1)-S(2a)	123.7(1)
S(3)-Zn(2)-S(5)	128.6(1)	S(3)-Zn(2)-S(4)	77.8(1)
S(3)-Zn(2)-S(6)	123.5(1)	S(4)-Zn(2)-S(5)	121.9(1)
S(5)-Zn(2)-S(6)	77.6(1)	S(4)-Zn(2)-S(6)	135.6(1)
Zn(1)-S(2)-C(1)	82.2(2)	Zn(1)-S(1)-C(1)	82.7(2)
Zn(2)-S(4)-C(5)	81.6(2)	Zn(2)-S(3)-C(5)	82.9(2)
Zn(2)-S(6)-C(9)	82.3(2)	Zn(2)-S(5)-C(9)	82.1(2)
S(1)-C(1)-C(2)	121.5(5)	S(1)-C(1)-S(2)	116.9(4)
C(1)-C(2)-C(3)	121.6(6)	S(2)-C(1)-C(2)	121.6(5)
C(3)-C(2)-C(4)	117.3(6)	C(1)-C(2)-C(4)	121.0(6)
N(2)-C(4)-C(2)	177.5(8)	N(1)-C(3)-C(2)	178.8(7)
S(3)-C(5)-C(6)	121.4(5)	S(3)-C(5)-S(4)	117.3(4)
C(5)-C(6)-C(7)	121.9(6)	C(4)-C(5)-C(6)	121.3(5)
C(7)-C(6)-C(8)	115.6(6)	C(5)-C(6)-C(8)	122.4(6)
N(4)-C(8)-C(6)	177.7(8)	N(3)-C(7)-C(6)	177.4(7)
S(5)-C(9)-C(10)	121.9(5)	S(5)-C(9)-C(6)	118.0(4)
C(9)-C(10)-C(11)	119.1(6)	S(6)-C(9)-C(10)	120.1(5)
C(11)-C(10)-C(12)	117.6(6)	C(9)-C(10)-C(12)	123.3(7)
N(6)-C(12)-C(10)	178.0(9)	N(5)-C(11)-C(10)	176.5(8)

Structure of the complex anion is similar to that of $Pt(i\text{-mnt})_2^{2-}$.[1] All the atoms form a plane; deviations of Pd and four S atoms from the plane are 0, and those of other atoms are not larger than 0.35 Å. In the complex anion, Pd sits on a centre of symmetry and is coordinated by four S atoms. The four Pd-S bond distances are

Table 5 Selected bond lengths and angles for $(Et_4N)_2Pd(i\text{-mnt})_2$ *(2)* (Å and degrees).

Pd-S(1)	2.323(1)	Pd-S(2)	2.324(1)
S(1)-C(1)	1.723(3)	S(2)-C(1)	1.725(3)
N(1)-C(3)	1.136(5)	N(2)-C(4)	1.143(5)
C(1)-C(2)	1.375(4)	C(2)-C(3)	1.418(4)
C(2)-C(4)	1.417(5)		
S(1)-Pd-S(2)	75.2(1)	S(1)-Pd-S(1a)	180.0(1)
S(2)-Pd-S(1a)	104.8(1)	Pd-S(1)-C(1)	87.1(1)
Pd-S(2)-C(1)	87.0(1)	S(1)-C(1)-S(2)	110.6(2)
S(1)-C(1)-C(2)	124.7(2)	S(2)-C(1)-C(2)	124.7(2)
C(1)-C(2)-C(3)	120.4(3)	C(1)-C(2)-C(4)	122.0(3)
C(3)-C(2)-C(4)	117.6(3)	N(1)-C(3)-C(2)	179.8(5)
N(2)-C(4)-C(2)	179.6(4)		

Table 6 Equations of least-squares planes in $Zn(i\text{-mnt})_2^{2-}$

Atom	Dev. from plane (Å)	Atom	Dev. from plane (Å)
Plane 1: 33.766x + 6.952y − 2.697z − 1.0998 = 0			
Zn1	0.000	C1	−0.0901
S1	0.000	C2	−0.2353
S2	0.000	C3	−0.4074
N1	−0.551	C4	−0.1308
N2	−0.0126		
Plane 2: 33.766x − 6.952y − 2.697z + 2.4487 = 0			
symmetry-equivalent to Plane 1			
Plane 3: 30.721x −6.987y −8.745z + 3.0394 = 0			
Zn2	0.0000	C5	−0.1244
S3	0.0000	C6	−0.3353
S4	0.0000	C7	−0.3844
N3	−0.4363	C8	−0.5607
N4	−0.7310		
Plane 4: 34.468x + 6.865y − 0.220z − 10.3870 = 0			
Zn2	0.0000	C9	−0.0076
S5	0.0000	C10	0.0003
S6	0.0000	C11	−0.0749
N5	−0.0894	C12	0.0971
N6	0.1939		

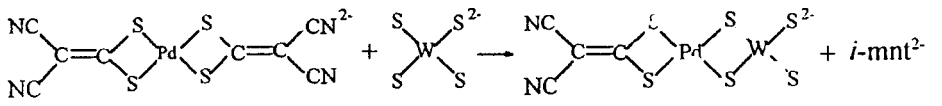
identical at 2.323(1)Å, which is comparable to those found in Pd complexes of other monovalent 1,1-dithiolato anion ligands.[14]

Comparison of the structure features of (1) and (2)

The complex anion in *$(Bu_4N)_2Zn(i\text{-mnt})_2$ (1)* is tetrahedral, while that in *$(Et_4N)_2Pd(i\text{-mnt})_2$ (2)* is planar as mentioned above. The three S-C-S angles in *(1)* are 116.9(4), 117.3(4) and 118.0(4)°, which differ from 122.8(3)° as found in sodium salts of *i*-mnt.[24] This indicates covalent bonding of the ligand with metal in *(1)*, even though the bonding is not as strong as in *(2)*, in which the S-C-S angle is 110.6(2)°. The three S-Zn-S angles in *(1)* are 78.0(1), 77.8(1) and 77.6(1)°. Comparing them with the S-Pd-S angle of 75.2(1)° in *(2)*, significantly less covalent bonding can be seen for Zn-S bonds. The C—C, C=C and C≡N bond lengths primarily maintain unchanged before[24] and after the complexes form. These reveal that bonding in the ligand within the complex anions is comparable to that in the free ligand *i*-mnt with delocalization of the π-electron system.

Reaction of (2) with $(Et_4N)_2WS_4$

Reaction of *(2)* with $(Et_4N)_2WS_4$ affords a crystalline product, $(Et_4N)_2WS_4Pd(i\text{-mnt})$, as shown by elemental analyses.



One *i*-mnt ligand is substituted by WS_4^{2-} which acts as a bidentate ligand. The IR spectrum shows that the product contains *i*-mnt and WS_4^{2-} with bands at 2202 cm^{-1} ($\nu C{\equiv}N$), 488 ($\nu W{-}S_t$) and 443 cm^{-1} ($\nu W{-}S_{br}$). The former is comparable to that (2199 cm^{-1}) found in *(2)* and the latter to those found in $Ag_3WS_4Br(PPh_3)_3 \cdot H_2O$.[21] A structure determination of the product is being performed.

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SUPPLEMENTARY DATA

Full lists of atomic positions, bond lengths and angles, thermal parameters, observed and calculated structure factors are available from the authors upon request.

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