Structural Studies of Metal Complexes with Sulphur-containing Bidentate Ligands. Part I. Crystal and Molecular Structures of Trimeric Bis(dithiobenzoato)-nickel(II) and -palladium(II)

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The crystal and molecular structures of the title compounds have been determined by the heavy-atom method and refined by anisotropic least-squares methods to final R of 0.088 (Ni) and 0.051 (Pd). The nickel complex crystallises in space group $P2_1/n$, with Z = 6 in a unit cell of dimensions a = 5.809(10), b = 17.306(10), c = 21.392(10) Å, β = 93° 56′ ± 5′. The palladium complex crystallises in space group $P2_1/c$, with Z = 6 in a unit cell of dimensions a = 5.943(10), b = 12.662(10), c = 28.707(10) Å, β = 93° 36′ ± 10′.

Although the two structures are similar, both consisting of trimeric units, in which the metal co-ordination is essentially square-planar, there are differences in the metal–sulphur intratrimer interactions.

MANY nickel(II) complexes of bidentate dithio-ligands are reported in the crystallographic literature, and much information is available on the steric and structural features of different classes of complexes, the characteristics of the ligands R-CS_2^-, the type of Ni–S bond present, and on the correlation between molecular structure and crystal packing. By contrast, the structures of palladium(II) complexes with the same, or similar, ligands have been little investigated.

We have carried out structure determinations for several palladium(II) dithiocarboxylates in order to study the Pd–S bond in four-membered chelate rings and to bring to light any differences between the nickel(II) and palladium(II) complexes with the same ligands. The first part of this work compares the structures of two such compounds, already reported briefly.[1,2]

EXPERIMENTAL

The title compounds were prepared following the methods of ref. 3. Crystals were stable in air and in the X-ray beam.

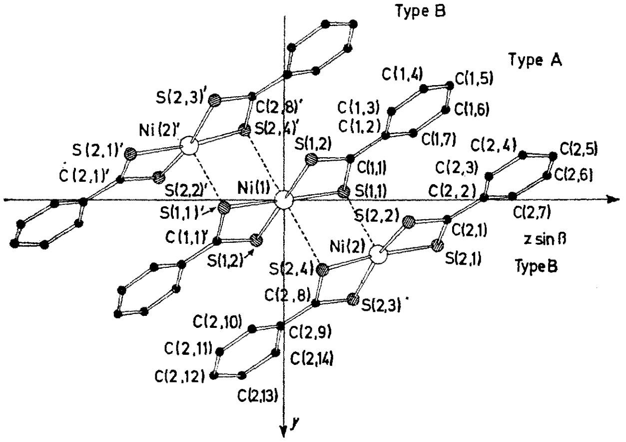

FIGURE 1 [100] Projection of the bis(dithiobenzoato)nickel(II) trimer

Crystal Data, Intensity Measurements, and Corrections.— Unit-cell dimensions were determined by an improved version of Christ's method[4] from zero-layer Weissenberg films taken about the a axis, and precession photographs taken about the b axis, using reflections from mainly Cu-K_{α_1} radiation (λ = 1.5406 Å).

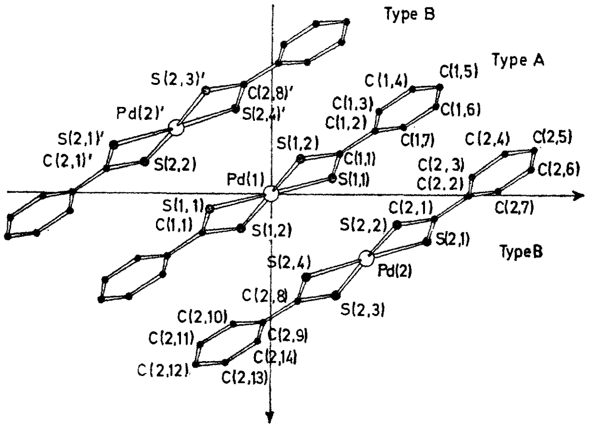

FIGURE 2 [100] Projection of the bis(dithiobenzoato)-palladium(II) trimer

Bis(dithiobenzoato)nickel(II). $C_{14}H_{10}NiS_4$, M = 365.202, deep blue monoclinic prisms, a = 5.809(10), b = 17.306(5), c = 21.392(10) Å, β = 93° 56′ ± 10′, U = 2 146 Å^3, D_m = 1.69 g cm^{-3} (by flotation), Z = 6, D_c = 1.69 g cm^{-3}; $F(000)$ = 1 104.5. μ(Cu-K_α) = 69 cm^{-1}. Space group $P2_1/n$ from systematic absences. The intensities of 1 768 reflections above film background were collected from equi-inclination Weissenberg layers 0—5 kl, and precession layers h0—2l, to give 1 621 independent reflections (*ca.* 34% of those possible with Cu-K_α radiation).

Bis(dithiobenzoato)palladium(II). $C_{14}H_{10}PdS_4$, M = 412.892, dark red-violet monoclinic prisms, a = 5.943(10), b = 12.662(5), c = 28.707(10) Å, β = 93° 36′ ± 10′, U = 2 156 Å^3, D_m = 1.88 g cm^{-3} (by flotation), Z = 6, D_c = 1.909 g cm^{-3}, $F(000)$ = 1 229.3. μ(Cu-K_α) = 160 cm^{-1}. Space group $P2_1/c$ from systematic absences. The intensities of 2 665 reflections above film background were collected from equi-inclination Weissenberg layers 0—5kl, and precession layers h0—2l to give 2 442 independent reflections (*ca.* 51% of those possible with Cu-K_α radiation).

For both structures intensity data were corrected for Lorentz and polarisation effects, and for spot extension.[5]

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[1] M. Bonamico and G. Dessy, *Chem. Comm.*, 1968, 483.

[2] M. Bonamico, G. Dessy, and V. Fares, *Chem. Comm.*, 1969, 324.

[3] C. Furlani and M. L. Luciani, *Inorg. Chem.*, 1968, **7**, 1586.

[4] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca Sci.*, 1963, **33**, 1113.

[5] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

An absorption correction was introduced in the case of the palladium complex only. First scaling of observed structure amplitudes was performed by correlating common reflections in different layers. Final scaling, with an independent scale factor for each layer, was carried out at the end of the isotropic least-squares refinement, after introduction of the hydrogen atoms in the structure-factor calculation.

TABLE 1

Co-ordinates ($\times 10^4$) and temperature factors,* with standard deviations in parentheses, for the nickel compound

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Ni(1)	0(0)	0(0)	0(0)	386(14)	−57(7)	−18(5)	47(2)	6(2)	14(1)
Ni(2)	−539(4)	1 058(2)	1 514(1)	350(10)	−25(5)	−10(4)	46(1)	3(2)	18(1)
S(1,1)	1 676(6)	−159(3)	960(2)	352(15)	−30(8)	−14(5)	49(2)	0(2)	16(1)
S(1,2)	−2 469(6)	−779(2)	443(2)	346(15)	−31(7)	−14(5)	42(2)	−2(2)	18(1)
S(2,1)	1 188(7)	887(3)	2 463(2)	365(14)	−47(8)	−14(6)	49(2)	−1(2)	18(1)
S(2,2)	−3 221(7)	433(3)	2 008(2)	313(14)	−5(8)	3(6)	51(2)	4(2)	23(1)
S(2,3)	1 688(7)	1 939(3)	1 104(2)	430(16)	−62(8)	−31(6)	44(2)	2(2)	20(1)
S(2,4)	−2 504(7)	1 354(3)	624(2)	373(16)	−64(8)	−36(6)	54(2)	15(2)	22(1)
C(1,1)	−513(24)	−797(8)	1 062(7)	294(50)	1(25)	21(20)	36(7)	−7(8)	19(4)
C(1,2)	−674(27)	−1 256(9)	1 634(8)	420(66)	58(31)	23(28)	32(7)	2(9)	26(6)
C(1,3)	1 178(29)	−1 303(10)	2 082(8)	507(73)	−2(31)	−19(28)	37(6)	11(9)	20(5)
C(1,4)	1 070(32)	−1 772(11)	2 609(8)	591(70)	24(35)	−83(28)	45(9)	26(10)	24(5)
C(1,5)	−894(36)	−2 225(11)	2 666(9)	692(92)	53(44)	73(34)	47(9)	21(11)	21(5)
C(1,6)	−2 795(29)	−2 165(11)	2 234(8)	478(83)	−49(40)	24(31)	47(8)	5(10)	21(5)
C(1,7)	−2 659(29)	−1 717(9)	1 717(8)	535(68)	−33(34)	−15(27)	28(7)	−12(9)	22(5)
C(2,1)	−1 195(23)	395(9)	2 630(7)	276(48)	11(26)	8(20)	37(6)	−7(8)	18(4)
C(2,2)	−1 554(26)	−40(9)	3 201(8)	380(61)	−37(29)	7(23)	37(7)	0(9)	20(5)
C(2,3)	282(26)	−53(9)	3 673(7)	428(61)	−10(35)	30(25)	40(9)	8(11)	12(5)
C(2,4)	57(30)	−463(10)	4 223(8)	533(77)	−5(36)	26(32)	41(9)	−3(11)	26(6)
C(2,5)	−1 984(37)	−845(12)	4 304(10)	653(93)	−21(45)	113(37)	55(10)	17(12)	26(6)
C(2,6)	−3 791(31)	−854(11)	3 831(10)	486(77)	−69(36)	4(31)	44(8)	12(11)	32(5)
C(2,7)	−3 534(28)	−452(11)	3 299(8)	368(61)	26(29)	2(22)	51(7)	11(8)	24(4)
C(2,8)	−374(22)	1 997(8)	520(6)	344(52)	−32(24)	−10(20)	25(6)	−6(7)	15(4)
C(2,9)	−229(29)	2 479(10)	−41(8)	536(72)	34(33)	−20(26)	35(7)	2(8)	18(4)
C(2,10)	1 666(26)	2 964(10)	−115(8)	387(58)	−65(31)	20(24)	38(7)	3(9)	23(5)
C(2,11)	1 728(32)	3 426(10)	−659(10)	501(74)	−105(36)	64(35)	37(8)	5(11)	38(7)
C(2,12)	−112(32)	3 417(9)	−1 108(9)	596(82)	−58(34)	28(32)	27(7)	8(9)	26(6)
C(2,13)	−1 982(28)	2 955(11)	−1 023(8)	441(69)	−23(35)	−23(28)	43(8)	14(11)	29(6)
C(2,14)	−2 129(26)	2 511(9)	−505(7)	405(58)	18(28)	−17(23)	30(6)	19(8)	21(4)
H(1,3) †	2 607	−996	2 024						
H(1,4)	2 372	−1 784	2 940						
H(1,5)	−938	−2 598	3 022						
H(1,6)	−4 250	−2 452	2 304						
H(1,7)	−3 974	−1 710	1 390						
H(2,3)	1 741	235	3 610						
H(2,4)	1 354	−480	4 555						
H(2,5)	−2 183	−1 122	4 707						
H(2,6)	−5 237	−1 152	3 888						
H(2,7)	−4 823	−452	2 964						
H(2,10)	2 969	2 984	215						
H(2,11)	3 100	3 760	−720						
H(2,12)	−74	3 746	−1 491						
H(2,13)	−3 283	2 946	−1 355						
H(2,14)	−3 560	2 206	−447						

* For non-hydrogen atoms, exponential coefficients b_{ij} are defined by $T = \exp 10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$. † $B = 5$ Å².

Determination and Refinement of the Structures.—Since $Z = 6$ for both structures, at least two (crystallographically equivalent) must be centrosymmetric (type A in Figures 1 and 2). The three-dimensional Patterson syntheses showed that the other four (type B) are in general positions and crystallographically equivalent. The positions of all non-hydrogen atoms were found by successive Fourier syntheses. The positional and isotropic thermal parameters of the non-hydrogen atoms ($\bar{B}$ 3.5 Å² by Wilson's method) were refined by several cycles of 4 × 4 block-diagonal least-squares. At this stage R was 0.135 for the nickel and 0.103 for the palladium complex. Hydrogen atoms were then included at calculated positions (C–H 1.00 Å), with the average isotropic temperature factor of the phenyl group atoms (B 5.0 Å² for the Ni complex and 4.5 Å² for the Pd complex). A new scaling (see earlier) and the introduction of anisotropic thermal motion for all non-hydrogen atoms brought R to 0.088(Ni) and 0.051 (Pd). The weighting scheme $w = (a + b|F_o| + c|F_o|^2)^{-1}$ was used throughout the refinements, where $a = 1.50$, $b = 1.00$, and $c = 0.002$ for the Ni and $a = 1.50$, $b = 1.00$, and $c = 0.0015$ for the Pd complex.

Tables 1 and 2 give the final atomic parameters and their standard deviations, within the crystal chemical units. Observed and calculated structure factors, based on the final atomic parameters, are listed in Supplementary Publication No. SUP 21379 (6 pp., 1 microfiche).* Bond distances and angles, with their standard deviations, are listed in Tables 3 and 4.

Calculations.—Calculations were carried out on the IBM 7040 computer at Rome University. Intensity corrections, scaling, Wilson plots, Fourier syntheses, and interatomic

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

distances and angles were calculated with programs written by Domenicano and Vaciago.[6] Programs written by Albano *et al.*[7] were used for the structure-factor calculations and the least-squares refinements and a program by Spagna [8] for the calculation of least-squares planes. Scattering factors for hydrogen atoms were those of ref. 9, and neutral atomic scattering factors, corrected for anomalous dispersion in the case of nickel, palladium, and sulphur,[10] from ref. 11.

DISCUSSION

Comparison of the two elementary cells shows that the values of *a* and β match, whilst the lengths of *b* and *c* and the space group differ ($P2_1/n$ for the Ni complex and $P2_1/c$ for the Pd complex). The fact that despite these differences similar trimers are found, though with different packing (Figures 3 and 4), suggests that intratrimer interactions are important and intertrimer contacts relatively unimportant. Each trimer consists of one molecule of type A linked centrosymmetrically to two molecules of type B *via* metal–sulphur bridges, the three molecules being virtually parallel (Figures 1 and 2).

There is a striking difference between the trimers. In the palladium trimer, both the A and B molecules are quite planar, the largest deviation from the least-squares plane being 0.13 Å, whilst in the nickel trimer the B molecule shows significant deviations from planarity: atoms Ni(2) and S(2,4) are displaced from the mean plane of B by 0.36 and 0.32 Å (see Table 5), approaching S(1,1) and Ni(1), respectively.

TABLE 2

Co-ordinates (× 10^4) and temperature factors,* with standard deviations in parentheses, for the palladium compound

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Pd(1)	0(0)	0(0)	0(0)	190(3)	5(2)	7(1)	73(1)	0(0)	9(0)
Pd(2)	1 506(1)	1 722(1)	1 155(0)	202(2)	15(2)	11(1)	74(0)	2(0)	9(0)
S(1,1)	−1 159(4)	−419(2)	739(1)	201(7)	40(6)	18(2)	102(2)	5(1)	12(0)
S(1,2)	2 982(4)	−933(2)	363(1)	204(7)	16(6)	18(2)	89(2)	4(1)	11(0)
S(2,1)	324(4)	1 250(2)	1 890(1)	222(7)	31(6)	20(2)	97(2)	3(1)	11(0)
S(2,2)	4 526(4)	822(2)	1 522(1)	208(7)	2(6)	24(2)	98(2)	5(1)	13(0)
S(2,3)	−1 418(4)	2 692(2)	793(1)	241(7)	18(6)	22(2)	95(2)	0(1)	11(0)
S(2,4)	2 764(4)	2 224(2)	436(1)	234(7)	36(7)	30(3)	111(2)	9(1)	13(0)
C(1,1)	1 333(16)	−1 065(7)	823(3)	256(30)	61(22)	11(10)	67(6)	0(4)	11(1)
C(1,2)	1 947(15)	−1 679(7)	1 247(3)	249(27)	104(20)	2(9)	63(5)	3(4)	10(1)
C(1,3)	373(17)	−1 774(8)	1 597(3)	302(32)	17(26)	10(10)	89(7)	9(5)	10(1)
C(1,4)	831(19)	−2 341(9)	1 992(4)	356(38)	8(29)	16(12)	95(8)	8(6)	13(1)
C(1,5)	2 918(19)	−2 853(8)	2 039(4)	359(37)	52(27)	15(13)	74(7)	14(5)	16(2)
C(1,6)	4 474(18)	−2 772(9)	1 699(4)	246(32)	18(26)	14(13)	79(7)	19(6)	19(2)
C(1,7)	4 004(16)	−2 194(8)	1 296(4)	205(28)	17(24)	10(10)	87(7)	10(5)	14(1)
C(2,1)	2 849(15)	650(7)	1 978(3)	197(26)	3(20)	4(9)	63(5)	6(4)	11(1)
C(2,2)	3 525(16)	26(8)	2 396(3)	254(31)	36(23)	17(11)	71(6)	7(5)	11(1)
C(2,3)	1 994(17)	−86(8)	2 753(4)	300(33)	27(26)	18(12)	75(7)	1(5)	15(1)
C(2,4)	2 563(22)	−704(9)	3 140(4)	478(45)	23(32)	16(14)	85(8)	11(6)	14(1)
C(2,5)	4 661(20)	−1 199(9)	3 174(4)	414(41)	23(29)	5(14)	74(7)	14(6)	16(2)
C(2,6)	6 127(18)	−1 091(9)	2 832(4)	267(35)	70(26)	12(14)	81(7)	0(7)	23(2)
C(2,7)	5 564(17)	−475(8)	2 432(4)	296(33)	36(24)	21(11)	70(6)	2(5)	15(1)
C(2,8)	273(16)	2 848(7)	339(3)	238(29)	70(22)	2(10)	69(6)	15(4)	11(1)
C(2,9)	−352(18)	3 440(9)	−85(4)	336(35)	47(27)	8(11)	70(6)	12(5)	12(1)
C(2,10)	−2 404(18)	3 945(9)	−144(4)	333(34)	20(27)	32(12)	79(7)	1(6)	17(2)
C(2,11)	−2 883(19)	4 531(9)	−541(4)	312(36)	22(29)	34(14)	88(8)	11(6)	19(2)
C(2,12)	−1 370(20)	4 579(10)	−893(4)	390(40)	21(33)	14(14)	104(9)	2(7)	14(2)
C(2,13)	679(21)	4 064(10)	−843(4)	410(42)	59(32)	20(14)	99(8)	2(6)	13(1)
C(2,14)	1 210(18)	3 494(9)	−447(3)	334(35)	45(29)	7(11)	94(8)	1(5)	10(1)
H(1,3) †	−1 253	−1 379	1 546						
H(1,4)	−376	−2 396	2 262						
H(1,5)	3 334	−3 327	2 350						
H(1,6)	6 095	−3 172	1 751						
H(1,7)	5 211	−2 145	1 026						
H(2,3)	369	315	2 722						
H(2,4)	1 390	−802	3 414						
H(2,5)	5 134	−1 680	3 479						
H(2,6)	7 759	−1 486	2 867						
H(2,7)	6 736	−400	2 157						
H(2,10)	−3 633	3 881	121						
H(2,11)	−4 468	4 965	−581						
H(2,12)	−1 809	5 027	−1 210						
H(2,13)	1 863	4 112	−1 117						
H(2,14)	2 818	3 080	−406						

* See footnote (1) for Table 1. † $B = 4.50$ Å^2.

It thus appears that there is a strong interaction between type A and B molecules of the nickel trimers. In fact, Ni(1)–S(2,4) and Ni(2)–S(1,1) distances are 3.11 and 2.77 Å, 0.68 and 0.34 Å greater than the sum of the

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[6] A. Domenicano and A. Vaciago, unpublished work.

[7] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

[8] R. Spagna, unpublished work.

[9] H. P. Hanson, F. Herman, J. D. Lea, and S. Skilmann, *Acta Cryst.*, 1964, **17**, 1040.

[10] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[11] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

covalent radii (2.43 Å). In addition, the plane of Ni(1) and the four S atoms in type A is twisted with respect to the rest of the molecule, thus displacing S(1,1) and Ni(2) 0.34 Å towards each other (see Figure 5). Instead, in the palladium trimers, Pd(1)–S(2,4) and Pd(2)–S(1,1) distances of 3.46 and 3.32 Å are proportionately larger, being 0.92 and 0.78 Å longer than the sum of the covalent radii (2.54 Å), and the corresponding displacement

TABLE 3

Bond distances (Å) and angles (°), with standard deviations in parentheses, for the nickel compound

(*a*) Distances

Ni(1)–S(1,1)	2.229(4)	C(1,4)–C(1,5)	1.40(2)
Ni(1)–S(1,2)	2.227(3)	C(1,5)–C(1,6)	1.40(2)
Ni(1)–S(2,4)	3,108(5)	C(1,6)–C(1,7)	1.36(2)
Ni(2)–S(2,1)	2.221(5)	C(2,1)–C(2,2)	1.46(2)
Ni(2)–S(2,2)	2.223(5)	C(2,2)–C(2,3)	1.42(2)
Ni(2)–S(2,3)	2.218(5)	C(2,2)–C(2,7)	1.38(2)
Ni(2)–S(2,4)	2.212(5)	C(2,3)–C(2,4)	1.39(2)
Ni(2)–S(1,1)	2.776(5)	C(2,4)–C(2,5)	1.38(2)
S(1,1)–C(1,1)	1.71(1)	C(2,5)–C(2,6)	1.41(2)
S(1,2)–C(1,1)	1.69(2)	C(2,6)–C(2,7)	1.35(2)
S(2,1)–C(2,1)	1.68(1)	C(2,8)–C(2,9)	1.47(2)
S(2,2)–C(2,1)	1.72(2)	C(2,9)–C(2,10)	1.40(2)
S(2,3)–C(2,8)	1.67(1)	C(2,9)–C(2,14)	1.43(2)
S(2,4)–C(2,8)	1.69(1)	C(2,10)–C(2,11)	1.41(2)
C(1,1)–C(1,2)	1.47(2)	C(2,11)–C(2,12)	1.39(2)
C(1,2)–C(1,3)	1.39(2)	C(2,12)–C(2,13)	1.37(2)
C(1,2)–C(1,7)	1.42(2)	C(2,13)–C(2,14)	1.36(2)
C(1,3)–C(1,4)	1.40(2)		

(*b*) Angles

S(1,1)–Ni(1)–S(1,2)	77.7(1)	C(1,2)–C(1,3)–C(1,4)	121(1)
S(2,4)–Ni(1)–S(1,1)	83.4(1)	C(1,3)–C(1,4)–C(1,5)	119(2)
S(2,4)–Ni(1)–S(1,1)′	96.6(1)	C(1,4)–C(1,5)–C(1,6)	121(2)
S(2,4)–Ni(1)–S(1,2)	86.5(1)	C(1,5)–C(1,6)–C(1,7)	119(1)
S(2,4)–Ni(1)–S(1,2)′	93.5(1)	C(1,2)–C(1,7)–C(1,6)	121(2)
S(2,1)–Ni(2)–S(2,2)	77.8(2)	S(2,1)–C(2,1)–C(2,2)	127(1)
S(2,3)–Ni(2)–S(2,4)	77.4(2)	S(2,2)–C(2,1)–C(2,2)	123(1)
S(1,1)–Ni(2)–S(2,1)	95.5(2)	C(2,1)–C(2,2)–C(2,3)	117(1)
S(1,1)–Ni(2)–S(2,2)	101.2(2)	C(2,1)–C(2,2)–C(2,7)	123(1)
S(1,1)–Ni(2)–S(2,3)	93.0(1)	C(2,3)–C(2,2)–C(2,7)	119(1)
S(1,1)–Ni(2)–S(2,4)	92.0(2)	C(2,2)–C(2,3)–C(2,4)	120(1)
Ni(1)–S(1,1)–C(1,1)	85.2(6)	C(2,3)–C(2,4)–C(2,5)	120(2)
Ni(1)–S(1,2)–C(1,1)	85.8(5)	C(2,4)–C(2,5)–C(2,6)	121(2)
Ni(2)–S(2,1)–C(2,1)	86.2(6)	C(2,5)–C(2,6)–C(2,7)	119(2)
Ni(2)–S(2,2)–C(2,1)	85.4(5)	C(2,2)–C(2,7)–C(2,6)	120(1)
Ni(2)–S(2,3)–C(2,8)	86.0(5)	S(2,3)–C(2,8)–C(2,9)	124(1)
Ni(2)–S(2,4)–C(2,8)	85.7(5)	S(2,4)–C(2,8)–C(2,9)	124(1)
S(1,1)–C(1,1)–S(1,2)	110.7(8)	C(2,8)–C(2,9)–C(2,10)	122(1)
S(2,1)–C(2,1)–S(2,2)	110.4(8)	C(2,8)–C(2,9)–C(2,14)	120(1)
S(2,3)–C(2,8)–S(2,4)	110.9(8)	C(2,10)–C(2,9)–C(2,14)	118(1)
S(1,1)–C(1,1)–C(1,2)	123(1)	C(2,9)–C(2,10)–C(2,11)	120(2)
S(1,2)–C(1,1)–C(1,2)	126(1)	C(2,10)–C(2,11)–C(2,12)	120(2)
C(1,1)–C(1,2)–C(1,3)	121(1)	C(2,11)–C(2,12)–C(2,13)	119(2)
C(1,1)–C(1,2)–C(1,7)	121(2)	C(2,12)–C(2,13)–C(2,14)	123(2)
C(1,3)–C(1,2)–C(1,7)	118(2)	C(2,9)–C(2,14)–C(2,13)	119(1)

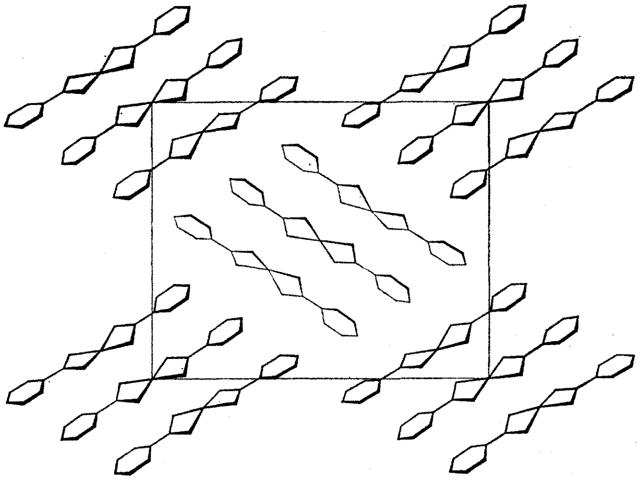

FIGURE 3 Schematic view of the unit cell of the Ni complex projected along *a*

TABLE 4

Bond distances (Å) and angles (°), with standard deviations in parentheses, for the palladium compound

(*a*) Distances

Pd(1)–S(1,1)	2.332(3)	C(1,4)–C(1,5)	1.40(2)
Pd(1)–S(1,2)	2.322(2)	C(1,5)–C(1,6)	1.39(2)
Pd(1)–S(2,4)	3.455(3)	C(1,6)–C(1,7)	1.38(1)
Pd(2)–S(2,1)	2.343(3)	C(2,1)–C(2,2)	1.47(1)
Pd(2)–S(2,2)	2.322(3)	C(2,2)–C(2,3)	1.42(2)
Pd(2)–S(2,3)	2.320(3)	C(2,2)–C(2,7)	1.37(1)
Pd(2)–S(2,4)	2.327(3)	C(2,3)–C(2,4)	1.38(2)
Pd(2)–S(1,1)	3.320(3)	C(2,4)–C(2,5)	1.39(2)
S(1,1)–C(1,1)	1.70(1)	C(2,5)–C(2,6)	1.36(2)
S(1,2)–C(1,1)	1.70(1)	C(2,6)–C(2,7)	1.41(1)
S(2,1)–C(2,1)	1.69(1)	C(2,8)–C(2,9)	1.46(1)
S(2,2)–C(2,1)	1.71(1)	C(2,9)–C(2,10)	1.38(2)
S(2,3)–C(2,8)	1.71(1)	C(2,9)–C(2,14)	1.44(1)
S(2,4)–C(2,8)	1.69(1)	C(2,10)–C(2,11)	1.38(2)
C(1,1)–C(1,2)	1.47(1)	C(2,11)–C(2,12)	1.40(2)
C(1,2)–C(1,3)	1.42(1)	C(2,12)–C(2,13)	1.38(2)
C(1,2)–C(1,7)	1.39(1)	C(2,13)–C(2,14)	1.37(2)
C(1,3)–C(1,4)	1.36(1)		

(*b*) Angles

S(1,1)–Pd(1)–S(1,2)	74.7(1)	C(1,2)–C(1,3)–C(1,4)	122.0(9)
S(2,4)–Pd(1)–S(1,1)	91.0(1)	C(1,3)–C(1,4)–C(1,5)	117.2(9)
S(2,4)–Pd(1)–S(1,1)′	89.0(1)	C(1,4)–C(1,5)–C(1,6)	121.6(9)
S(2,4)–Pd(1)–S(1,2)	85.4(1)	C(1,5)–C(1,6)–C(1,7)	121.2(9)
S(2,4)–Pd(1)–S(1,2)′	94.6(1)	C(1,2)–C(1,7)–C(1,6)	117.7(9)
S(2,1)–Pd(2)–S(2,2)	74.5(1)	S(2,1)–C(2,1)–C(2,2)	112.6(5)
S(2,3)–Pd(2)–S(2,4)	74.4(1)	S(2,2)–C(2,1)–C(2,2)	123.4(7)
S(1,1)–Pd(2)–S(2,1)	87.3(1)	C(2,1)–C(2,2)–C(2,3)	119.2(9)
S(1,1)–Pd(2)–S(2,2)	95.7(1)	C(2,1)–C(2,2)–C(2,7)	120.4(9)
S(1,1)–Pd(2)–S(2,3)	86.8(1)	C(2,3)–C(2,2)–C(2,7)	120.3(9)
S(1,1)–Pd(2)–S(2,4)	94.4(1)	C(2,2)–C(2,3)–C(2,4)	120.1(9)
Pd(1)–S(1,1)–C(1,1)	86.2(3)	C(2,3)–C(2,4)–C(2,5)	118.9(9)
Pd(1)–S(1,2)–C(1,1)	86.4(3)	C(2,4)–C(2,5)–C(2,6)	121.0(9)
Pd(2)–S(2,1)–C(2,1)	86.3(3)	C(2,5)–C(2,6)–C(2,7)	120.9(9)
Pd(2)–S(2,2)–C(2,1)	86.5(3)	C(2,2)–C(2,7)–C(2,6)	118.8(9)
Pd(2)–S(2,3)–C(2,8)	86.7(3)	S(2,3)–C(2,8)–C(2,9)	124.5(7)
Pd(2)–S(2,4)–C(2,8)	87.0(3)	S(2,4)–C(2,8)–C(2,9)	123.7(7)
S(1,1)–C(1,1)–S(1,2)	112.5(5)	C(2,8)–C(2,9)–C(2,10)	121.2(9)
S(2,1)–C(2,1)–S(2,2)	112.6(5)	C(2,8)–C(2,9)–C(2,14)	119.1(9)
S(2,3)–C(2,8)–S(2,4)	111.9(5)	C(2,10)–C(2,9)–C(2,14)	119.7(9)
S(1,1)–C(1,1)–C(1,2)	122.8(7)	C(2,9)–C(2,10)–C(2,11)	119.2(9)
S(1,2)–C(1,1)–C(1,2)	124.7(7)	C(2,10)–C(2,11)–C(2,12)	121.0(9)
C(1,1)–C(1,2)–C(1,3)	119.3(8)	C(2,11)–C(2,12)–C(2,13)	121.0(9)
C(1,1)–C(1,2)–C(1,7)	120.3(8)	C(2,12)–C(2,13)–C(2,14)	119.5(9)
C(1,3)–C(1,2)–C(1,7)	120.3(8)	C(2,9)–C(2,14)–C(2,13)	120.0(9)

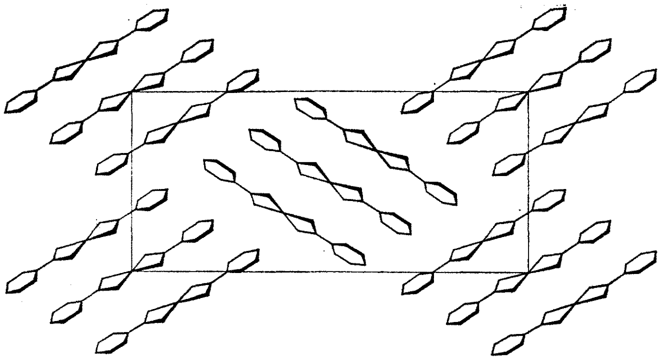

FIGURE 4 Schematic view of the unit cell of the Pd complex projected along *a*

TABLE 5

Results of least-squares planes calculations. Equations of planes, in the form $Ax + By + Cz + D = 0$, are referred to the crystallographic axes

Nickel complex				Palladium complex			
Atoms defining the plane		Deviations (Å) from the plane		Atoms defining the plane		Deviations (Å) from the plane	
	Plane (*a*)				Plane (*a*′)		
A	*B*	*C*	*D*	*A*	*B*	*C*	*D*
0.46879	−0.74881	−0.49959	−0.26865	0.37074	0.83127	0.39008	0.0000
	Ni(1)	0.00			Pd(1)	0.00	
	S(1,1)	0.10			S(1,1)	0.13	
	S(1,2)	−0.12			S(1,2)	−0.08	
	C(1,1)	−0.02			C(1,1)	−0.09	
	C(1,2)	0.04			C(1,2)	0.06	
	C(1,3)	0.07			C(1,3)	0.00	
	C(1,4)	0.08			C(1,4)	0.05	
	C(1,5)	−0.05			C(1,5)	−0.08	
	C(1,6)	−0.06			C(1,6)	−0.03	
	C(1,7)	−0.05			C(1,7)	−0.02	
	Plane (*b*)				Plane (*b*′)		
0.44269	−0.78830	−0.45668	3.42280	0.36667	0.82945	0.39753	3.46955
	Ni(2)	−0.36			Pd(2)	−0.01	
	S(2,1)	−0.11			S(2,1)	0.07	
	S(2,2)	−0.04			S(2,2)	0.12	
	S(2,3)	−0.13			S(2,3)	−0.05	
	S(2,4)	−0.32			S(2,4)	0.03	
	C(2,1)	−0.01			C(2,1)	0.09	
	C(2,2)	0.04			C(2,2)	0.06	
	C(2,3)	0.09			C(2,3)	0.02	
	C(2,4)	0.13			C(2,4)	−0.07	
	C(2,5)	0.13			C(2,5)	−0.09	
	C(2,6)	0.06			C(2,6)	−0.05	
	C(2,7)	0.02			C(2,7)	0.02	
	C(2,8)	−0.09			C(2,8)	−0.03	
	C(2,9)	−0.02			C(2,9)	−0.03	
	C(2,10)	0.08			C(2,10)	−0.01	
	C(2,11)	0.16			C(2,11)	−0.04	
	C(2,12)	0.19			C(2,12)	0.02	
	C(1,13)	0.12			C(2,13)	0.02	
	C(2,14)	0.06			C(2,14)	−0.05	

of S(1,1) and Pd(2) is only 0.14 Å. In this case, the trimer bridges do not appear to have induced significant buckling or out-of-plane distortions of the molecules.

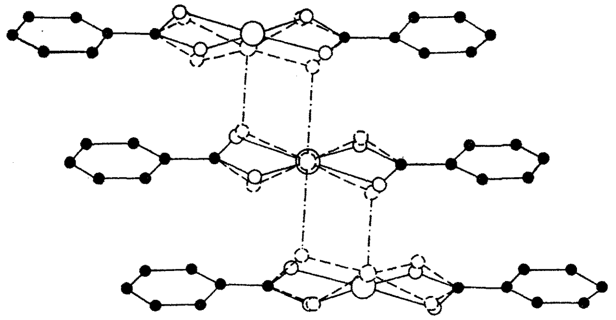

FIGURE 5 Superposition of the Ni and Pd trimers showing the out-of-plane distortion of Ni and S atoms with respect to the virtually planar Pd complex

Although Ni(1) in A should be regarded as having tetragonally distorted octahedral co-ordination, and Ni(2) in B as being five-co-ordinated, the Ni–S bond distances are in the range 2.21—2.23 Å, typical of Ni–S bonds in square-planar nickel complexes with four-membered chelate rings [Table 6 (refs. 12—21)]. This value, which depends on the type of ligand, and varies from 2.197(3) (mean) in bis(dithiocarbamato)nickel complexes to 2.232(5) Å (mean) in bis(dialkyl phosphorodithioato)- and bis(dialkyl- or diaryl-phosphinodithioato)-nickel complexes seems not to depend on the aggregation state of the chemical units in the crystal. In compounds (V)—(VII) of Table 6 the mean Ni–S bond lengths are identical (2.212—2.217 Å) although (V) [14] consists of discrete molecular units, (VI) [15] shows dimeric association, with two equivalent Ni–S bridge interactions of 2.706(5) Å, and the present nickel(II) complex is trimeric. Thus, the Ni–S bridge interactions appear to influence the nickel orbitals involved in the co-ordination bonds little, if at all. This suggests that the short metal–sulphur bridge is not the most important factor in

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[19] P. E. Jones, G. B. Ansell, and L. Katz, *Acta Cryst.*, 1969, **B25**, 1939.

[20] P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, 1968, **7**, 2625.

[21] L. Gastaldi and P. Porta, *Gazzetta*, 1971, 641.

determining the trimer association, but that interactions between the co-planar phenyl rings also play an important role.

In bis(dithiobenzoato)palladium(II) the mean Pd–S bond length [2.328(3) Å] is *ca.* 0.1 Å longer than the corresponding Ni–S distance, in agreement with the values of the covalent radii for nickel and palladium,[22] and the S–M–S angle is increased [74.5° (Pd) *vs.* 77.5° (Ni)].

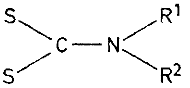
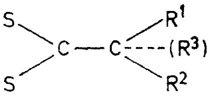
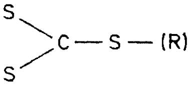
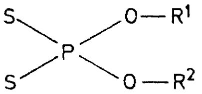
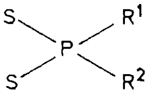
The Pd–S bond length may be compared with that [2.354(8) Å] for (*O*-ethyl phenylthiocarbamato)palladium (II).[21] The difference (0.026 Å) is probably significant and agrees with the greater strain in the four-membered chelate ring of the thiocarbamate (see Table 6).

The $(S_2CPh)^-$ ligand geometry is the same in both the complexes. The S–C bond lengths in each ligand do not differ significantly: values range from 1.67 to 1.72 Å (σ 0.01 Å) for the former and from 1.68 to 1.71 Å (σ 0.01 Å) for the latter, and agree with the literature data. The Ph–C distances (1.47—1.48 Å) indicate a partial double-bond character, which is consistent with the ligand planarity. All the geometrical features of the ligand are indicative of a high degree of conjugation over the whole complex molecules.

TABLE 6

Principal mean distances (Å), with estimated standard deviations in parentheses, and angles (°) in four-membered chelate rings of nickel(II) and palladium(II) complexes with different ligand classes

(*a*) Nickel compounds

Ligand type	Compounds	Ni–S	S–Ni–S	Ni–S–C	S–C–S
	(I) [a]	2.201(2)	79.0	85.0	110.0
	(II) [b]	2.203(2)	79.1	84.8	110.3
	(III) [c]	2.203(3)	79.3	85.0	109.0
	(IV) [d]	2.181(3)	79.3	86.0	109.5
	(V) [e]	2.212(5)	77.0	86.6	110.0
	(VI) [f]	2.217(5)	77.0	86.6	109.0
	(VII) [g]	2.217(5)	77.5	86.0	110.0
	(VIII) [h]	2.211(4)	78.5	84.3	112.8
					S–P–S
	(IX) [i]	2.222(2)	88.3	84.5	103
	(X) [j]	2.233(4)	88.5	84.5	103
	(XI) [k]	2.235(5)	87.7	85.5	101
	(XII) [l]	2.238(5)	88.0	85.0	101

(*b*) Palladium compounds

	Pd–S	S–Pd–S	Pd–S–C	S–C–S
(XIII) [m]	2.328(3)	74.5 °	86.3 °	112.3
		S–Pd–N		S–C–N
(XIV) [n]	2.354(8)	70.0 °	77.0 °	112.0

[a] Bis(diethyldithiocarbamato)nickel(II) (ref. 12). [b] Bis(dipropyldithiocarbamato)nickel(II) (ref. 13). [c] Bis(methylphenyldithiocarbamato)nickel(II) (J. M. Mastin, P. W. G. Newman, B. W. Robinson, and A. H. White, *J.C.S. Dalton*, 1972, 2233). [d] Bis(diisopropyldithiocarbamato)nickel(II) (P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 2239). [e] Dithiocumoato(trithioperoxycumoato)nickel(II) (ref. 14). [f] Bis(dithiopivalato)nickel(II) (ref. 15). [g] Bis(dithiobenzoato)nickel(II) (present work). [h] Di-μ-ethylthiolato-bis(ethyl trithiocarbonato)dinickel(II) (ref. 16). [i] Bis(dimethyl dithiophosphato)nickel(II) (ref. 17). [j] Bis(diethyl dithiophosphato)nickel(II) (ref. 18). [k] Bis(dimethyldithiophosphinato)nickel(II) (ref. 19). [l] Bis(diphenyldithiophosphinato)nickel(II) (ref. 20). [m] Bis(dithiobenzoato)palladium(II) (present work). [n] (*O*-Ethyl phenylthiocarbamato)palladium(II) (ref. 21).

[4/2717 *Received*, 30*th December*, 1974]

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