Journal of Organometallic Chemistry, 236 (1982) 273—280
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CRYSTAL AND MOLECULAR STRUCTURE OF $[\{Rh(C_5Me_5)\}_3Cl_5np_3]PF_6 \cdot 0.5\ C_3H_8O$

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(Received April 28th, 1982)

Summary

The crystal and molecular structure of the monoligand trimetallic complex $[\{Rh(C_5Me_5)\}_3Cl_5np_3]PF_6 \cdot 0.5\ C_3H_8O$ (np_3 = tris(2-diphenylphosphinoethyl)-amine) have been established by a single-crystal X-ray diffraction study. The cation of the complex contains two $Rh(C_5Me_5)Cl_2$ units each bound through the metal to one phosphorus atom of the ligand and a $Rh(C_5Me_5)Cl$ group in which the rhodium is bound to the third phosphorus atom and to the nitrogen of the tetradentate ligand.

The crystals are triclinic, space group $P\bar{1}$, with cell dimensions a 28.598(8), b 13.757(4), c 10.748(3) Å, α 90.69(4), β 96.67(4), γ 99.71(4)°, D_c 1.38 g cm^{-3} for $Z = 2$. The structure was solved by three dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional R value of 0.098.

Introduction

Transition metal complexes bound to organic π acceptors react with polydentate ligands involving tertiary Group V atoms as donors to give, under appropriate conditions, monoligand polymetallic complexes, in which the ligand acts as a holding center for several metal units [1].

We now describe the crystal structure of the complex $[\{Rh(C_5Me_5)\}_3Cl_5np_3]$-$PF_6$ obtained from the reaction between the tripod-like tetradentate ligand tris(2-diphenylphosphinoethyl)amine (np_3) [2], and the di-μ-chlorobis(chloro-(pentamethylcyclopentadienyl)rhodium complex, $[Rh_2(C_5Me_5)_2Cl_4]$ [3].

0022-328X/82/0000—0000/$02.75

Crystal data and data collection

Crystals obtained as previously described [4] from dichloromethane and ethanol were found to crumble once out of the mother liquor and were unsatisfactory for single-crystal diffraction work. The crystals obtained by recrystallization from dichloromethane and isopropanol crumbled more slowly during several days, but were suitable for X-ray investigation. The crystals have a parallelepiped shape and that used for data collection had dimensions 0.026 × 0.10 × 0.50 mm. The crystals are triclinic and belong to the space group $P\bar{1}$ with two $[\{Rh(C_5Me_5)\}_3Cl_5np_3]PF_6$ molecules in the unit cell, which has the following dimensions: a 28.598(8), b 13.757(4), c 10.748(3) Å, α 90.69(4), β 96.67(4), γ 99.71(4)°. Intensity data were collected on an automatic computer-controlled Philips diffractometer PW 1100 equipped with a graphite monochromator, using Mo-K_α radiation. All reflections with $6° \leqslant 2\theta \leqslant 40°$ were measured using the ω-2θ scan technique with a scan speed of 0.07 deg/s in a range of 0.7° in 2θ across the peak. Background times were taken equal to half the scan time on each side of the peak. During the collection of the data the intensities of three standard reflections smoothly decreased to about 85% of their initial values. The intensities of the reflections were therefore rescaled on the basis of the intensities of these standard reflections.

The intensity data were corrected for Lorentz, polarization, and absorption; the standard deviations $\sigma(I)$ were estimated as described elsewhere [5], with an instability factor equal to 0.03. A reflection was considered observed if the net intensity $I \geqslant 3\sigma(I)$. From the 7708 total reflections, only 2233 had intensity $I \geqslant 3\sigma(I)$. Atomic scattering factors were taken from ref. 6.

Structure solution and refinement

The ΔF Fourier maps showed the presence of solvent molecules, which from the IR data (ν(OH) 3350 cm^{-1}) and elemental analysis of the complex must be isopropanol. Due to disorder and to the low occupancy factor (0.5) of the solvating molecules only three non-hydrogen atoms could be located in these maps. The fourth non-hydrogen atom has therefore not been introduced. The three peaks were taken to refer to carbon atoms C(37)—C(39).

The positions of the three rhodium atoms were obtained from a Patterson synthesis. Except for the fluorine atoms of the one independent hexafluorophosphate anion, the other non-hydrogen atoms were located from successive F_o Fourier maps.

The asymmetric unit contains one complex cation $[\{Rh(C_5Me_5)\}_3Cl_5np_3]^+$ and two PF_6 anions. Each anion site has multiplicity 0.5 as deduced from the positions of the two phosphorus atoms which lie in two symmetry-independent inversion centres. One of the two anions is clearly shown in the F_o and ΔF maps, but the fluorine atoms of the second hexafluorophosphate anion could not be located due to disorder. This is consistent with the thermal factor for the central phosphorus atom; for this reason the fluorine atoms of this anion were not introduced into calculations.

The structure was refined by a full matrix least-squares program [7]. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight assigned to the

TABLE 1

POSITIONAL PARAMETERS ($\times 10^4$), ANISOTROPIC TEMPERATURE FACTORS[a] ($\times 10^3$)

(Estimated standard deviations between brackets)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	3654(2)	1057(3)	2676(5)	16(3)	18(3)	52(5)	0(3)	−3(3)	26(3)
Rh(2)	3063(2)	−2638(3)	6444(5)	48(4)	25(3)	48(5)	5(3)	−4(3)	29(3)
Rh(3)	1420(2)	2153(3)	1881(5)	25(4)	40(4)	67(5)	4(3)	−3(3)	33(3)
P(1)	3587(5)	1228(11)	529(16)	28(11)	36(11)	47(14)	−2(9)	7(9)	32(10)
P(2)	2846(6)	−2398(11)	4325(16)	58(13)	11(11)	53(15)	2(9)	−2(11)	23(10)
P(3)	1610(5)	902(11)	3265(15)	14(11)	43(11)	47(14)	7(9)	−2(10)	33(10)
Cl(1)	3961(5)	−371(10)	2181(14)	42(11)	48(11)	43(14)	17(9)	16(10)	28(10)
Cl(2)	2719(6)	−1265(11)	6953(15)	109(16)	42(12)	43(15)	18(11)	1(11)	29(11)
Cl(3)	3798(6)	−1620(11)	6137(15)	70(13)	65(12)	65(14)	−14(10)	−18(10)	60(11)
Cl(4)	1684(6)	1296(12)	261(16)	70(13)	78(13)	65(16)	43(11)	2(11)	31(12)
Cl(5)	2197(5)	3087(10)	2525(15)	18(10)	38(11)	94(16)	−1(8)	−23(10)	20(10)

[a] The form of the thermal ellipsoids is $\exp(-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{12}hka^{\star}b^{\star} + \ldots))$.

F_o values according to the expression $w = 1/\sigma^2(F_o)$. The phenyl groups were refined as rigid bodies with idealized geometry. The hydrogen atom contributions were not introduced into the calculations. Anisotropic temperature factors were used for the rhodium, chlorine and phosphorus atoms of the np$_3$ ligand; isotropic temperature factors were used for all the other atoms. The final refinement gave an R factor of 0.098, and R_w, defined as $[\Sigma w(|F_o| -$

TABLE 2

POSITIONAL ($\times 10^4$) AND THERMAL ($\times 10^3$) ISOTROPIC PARAMETERS

Atom	x	y	z	U (Å^2)
N	2857(16)	181(33)	2197(47)	35(15)
C(1)	2723(18)	165(35)	802(52)	19(14)
C(2)	3112(18)	130(37)	−107(51)	33(17)
C(3)	2858(18)	−931(37)	2562(51)	28(17)
C(4)	2998(16)	−1057(33)	4036(46)	18(14)
C(5)	2563(17)	664(33)	2995(47)	6(15)
C(6)	2048(17)	142(33)	2839(45)	31(15)
C(7)	4316(21)	1925(42)	3551(56)	68(19)
C(8)	4160(17)	1295(34)	4353(47)	47(15)
C(9)	3738(19)	1482(38)	4832(53)	38(17)
C(10)	3592(19)	2237(38)	3983(52)	27(17)
C(11)	3925(22)	2515(43)	3213(57)	51(21)
C(12)	4829(19)	1994(38)	2800(51)	58(18)
C(13)	4477(19)	503(39)	5049(52)	44(18)
C(14)	3499(20)	1017(41)	5939(55)	70(19)
C(15)	3224(17)	2839(35)	4350(47)	38(16)
C(16)	4012(16)	3510(34)	2357(46)	33(16)
C(17)	2845(21)	−4166(40)	6434(56)	44(18)
C(18)	3340(18)	−3968(35)	6674(51)	34(15)
C(19)	3441(18)	−3465(36)	7878(52)	30(16)
C(20)	2998(16)	−3256(33)	8329(48)	19(14)
C(21)	2623(20)	−3770(37)	7371(54)	40(18)
C(22)	2538(20)	−4973(42)	5375(56)	57(20)
C(23)	3686(19)	−4314(39)	5924(53)	54(19)
C(24)	3914(23)	−3083(45)	8550(60)	77(22)
C(25)	2946(20)	−2729(43)	9490(60)	82(21)
C(26)	2108(26)	−3789(50)	7649(65)	100(27)
C(27)	1152(21)	3544(44)	1263(67)	62(20)
C(28)	1088(20)	3407(43)	2400(65)	54(19)
C(29)	793(20)	2457(41)	2706(59)	67(19)
C(30)	650(23)	2067(48)	1383(68)	79(23)
C(31)	888(19)	2627(39)	411(58)	46(17)
C(32)	1433(19)	4303(39)	542(52)	48(18)
C(33)	1270(21)	4163(45)	3373(60)	89(21)
C(34)	556(21)	2132(42)	3806(58)	61(20)
C(35)	288(22)	1043(46)	957(58)	83(23)
C(36)	809(19)	2378(39)	−993(59)	71(19)
C(37) [a]	1036(46)	−661(96)	8748(126)	113(49)
C(38) [a]	1397(47)	−1643(94)	8872(126)	111(49)
C(39) [a]	845(47)	−2099(97)	8246(124)	112(50)
P(4)	5000	5000	0	119(12)
P(5)	0	5000	0	278(18)
F(1)	5044(19)	4176(38)	1135(49)	194(22)
F(2)	4477(22)	4444(45)	−504(58)	213(27)
F(3)	5251(23)	4460(48)	−1019(60)	232(29)

[a] These last carbon atoms belong to the isopropanol molecule.

TABLE 3

THERMAL ($\times 10^3$) AND DERIVED POSITIONAL PARAMETERS ($\times 10^4$) OF GROUP ATOMS

Atom	x	y	z	U (Å^2)
C(1,1)	4095(10)	1124(28)	−229(29)	18(14)
C(2,1)	4115(10)	243(28)	−863(29)	43(17)
C(3,1)	4519(10)	141(28)	−1436(29)	63(20)
C(4,1)	4903(10)	920(28)	−1376(29)	43(18)
C(5,1)	4883(10)	1802(28)	−743(29)	53(20)
C(6,1)	4479(10)	1904(28)	−169(29)	43(17)
C(1,2)	3367(12)	2321(20)	−117(34)	15(15)
C(2,2)	3520(12)	2715(20)	−1225(34)	41(18)
C(3,2)	3326(12)	3498(20)	−1768(34)	57(19)
C(4,2)	2979(12)	3886(20)	−1203(34)	41(17)
C(5,2)	2826(12)	3492(20)	−96(34)	45(17)
C(6,2)	3020(12)	2709(20)	447(34)	26(15)
C(1,3)	3132(14)	−3080(27)	3300(29)	33(17)
C(2,3)	3597(14)	−2685(27)	3088(29)	55(19)
C(3,3)	3849(14)	−3220(27)	2371(29)	58(18)
C(4,3)	3636(14)	−4150(27)	1865(29)	44(15)
C(5,3)	3171(14)	−4545(27)	2077(29)	60(21)
C(6,3)	2919(14)	−4010(27)	2794(29)	32(16)
C(1,4)	2206(9)	−2742(22)	3601(39)	31(15)
C(2,4)	1957(9)	−2648(22)	4629(39)	70(18)
C(3,4)	1458(9)	−2813(22)	4467(39)	143(26)
C(4,4)	1210(9)	−3072(22)	3278(39)	62(20)
C(5,4)	1459(9)	−3165(22)	2250(39)	64(17)
C(6,4)	1958(9)	−3000(22)	2411(39)	59(13)
C(1,5)	1092(10)	−93(22)	3314(41)	23(16)
C(2,5)	913(10)	−703(22)	2255(41)	29(17)
C(3,5)	500(10)	−1403(22)	2272(41)	49(19)
C(4,5)	266(10)	−1494(22)	3348(41)	39(18)
C(5,5)	444(10)	−884(22)	4407(41)	71(19)
C(6,5)	857(10)	−183(22)	4390(41)	31(16)
C(1,6)	1815(11)	1201(28)	4809(24)	41(15)
C(2,6)	1983(11)	531(28)	5642(24)	27(15)
C(3,6)	2141(11)	820(28)	6896(24)	26(15)
C(4,6)	2130(11)	1779(28)	7316(24)	60(18)
C(5,6)	1961(11)	2449(28)	6483(24)	57(20)
C(6,6)	1804(11)	2160(28)	5229(24)	39(18)

$|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, was 0.095. The final positional and thermal parameters are listed in Tables 1, 2 and 3. Tables of structure factors may be obtained from P.D.

Results and discussion

The molecular structure of $[\{Rh(C_5Me_5)\}_3Cl_5np_3]PF_6$ consists of discrete $[\{Rh(C_5Me_5)\}_3Cl_5np_3]^+$ cations, PF_6 anions, and solvating isopropanol molecules. Figure 1 shows a perspective view of the cation. Selected bond distances and angles are listed in Table 4.

The tetradentate np_3 ligand bridges three pentamethylcyclopentadienyl rhodium units through the terminal phosphorus atoms; two of the metal atoms complete their coordination spheres with two chlorine ions, while the other

TABLE 4

SELECTED BOND DISTANCES AND ANGLES

Distances (Å)			
Rh(1)—P(1)	2.301(17)	N—C(1)	1.50(7)
Rh(1)—Cl(1)	2.362(16)	N—C(3)	1.58(7)
Rh(1)—N	2.387(42)	N—C(5)	1.49(7)
Rh(1)—C(7)	2.16(5)	C(1)—C(2)	1.57(8)
Rh(1)—C(8)	2.16(5)	C(3)—C(4)	1.60(7)
Rh(1)—C(9)	2.35(6)	C(5)—C(6)	1.52(6)
Rh(1)—C(10)	2.17(6)	P(1)—C(2)	1.91(5)
Rh(1)—C(11)	2.07(6)	P(2)—C(4)	1.86(5)
Rh(2)—P(2)	2.323(18)	P(3)—C(6)	1.86(5)
Rh(2)—Cl(2)	2.357(18)	C(7)—C(8)	1.29(8)
Rh(2)—Cl(3)	2.380(16)	C(7)—C(11)	1.50(9)
Rh(2)—C(17)	2.09(5)	C(8)—C(9)	1.43(8)
Rh(2)—C(18)	2.12(5)	C(9)—C(10)	1.47(8)
Rh(2)—C(19)	2.21(5)	C(10)—C(11)	1.34(9)
Rh(2)—C(20)	2.21(5)	C(17)—C(18)	1.39(8)
Rh(2)—C(21)	2.16(5)	C(17)—C(21)	1.40(9)
Rh(3)—P(3)	2.375(16)	C(18)—C(19)	1.43(7)
Rh(3)—Cl(4)	2.348(19)	C(19)—C(20)	1.48(7)
Rh(3)—Cl(5)	2.391(13)	C(20)—C(21)	1.47(7)
Rh(3)—C(27)	2.26(6)	C(27)—C(28)	1.26(10)
Rh(3)—C(28)	2.20(6)	C(27)—C(31)	1.57(8)
Rh(3)—C(29)	2.19(6)	C(28)—C(29)	1.49(8)
Rh(3)—C(30)	2.19(6)	C(29)—C(30)	1.49(9)
Rh(3)—C(31)	2.24(6)	C(30)—C(31)	1.46(9)
Angles (°)			
P(1)—Rh(1)—Cl(1)	83.1(6)	C(5)—C(6)—P(3)	115.0(32)
P(1)—Rh(1)—N	82.3(13)	C(11)—C(7)—C(8)	106.1(53)
Cl(1)—Rh(1)—N	90.5(12)	C(7)—C(8)—C(9)	114.0(51)
P(2)—Rh(2)—Cl(2)	89.2(6)	C(8)—C(9)—C(10)	101.8(46)
P(2)—Rh(2)—Cl(3)	84.8(6)	C(9)—C(10)—C(11)	110.2(52)
Cl(2)—Rh(2)—Cl(3)	92.2(6)	C(10)—C(11)—C(7)	106.5(52)
P(3)—Rh(3)—Cl(4)	88.3(6)	C(21)—C(17)—C(18)	112.5(49)
P(3)—Rh(3)—Cl(5)	88.9(5)	C(17)—C(18)—C(19)	105.2(49)
Cl(4)—Rh(3)—Cl(5)	93.4(6)	C(18)—C(19)—C(20)	110.9(42)
C(1)—N—C(3)	106.1(38)	C(19)—C(20)—C(21)	102.7(43)
C(1)—N—C(5)	117.3(42)	C(20)—C(21)—C(17)	108.3(48)
C(3)—N—C(5)	111.2(41)	C(31)—C(27)—C(28)	110.4(51)
N—C(1)—C(2)	120.0(42)	C(27)—C(28)—C(29)	117.7(55)
C(1)—C(2)—P(1)	101.3(32)	C(28)—C(29)—C(30)	97.0(51)
N—C(3)—C(4)	113.1(39)	C(29)—C(30)—C(31)	116.1(49)
C(3)—C(4)—P(2)	106.5(30)	C(30)—C(31)—C(27)	98.0(50)
N—C(5)—C(6)	111.3(37)		

$Rh(C_5Me_5)$ moiety is bound to one chlorine atom and to the central nitrogen of the ligand; the tetradentate ligand is almost completely flattened in this monoligand trimetallic cation. The coordination geometry is approximately the same for each of the metal atoms and can be considered as distorted pseudo-octahedral, the pentamethylcyclopentadienyl ring occupying three coordination positions. Bond lengths and angles within each $Rh(C_5Me_5)Cl_2P$ unit (Table 4) are in the same range as those in monomeric pentamethylcyclopentadienyl rhodium(III) complexes having tertiary phosphines and two ions as ligands [8];

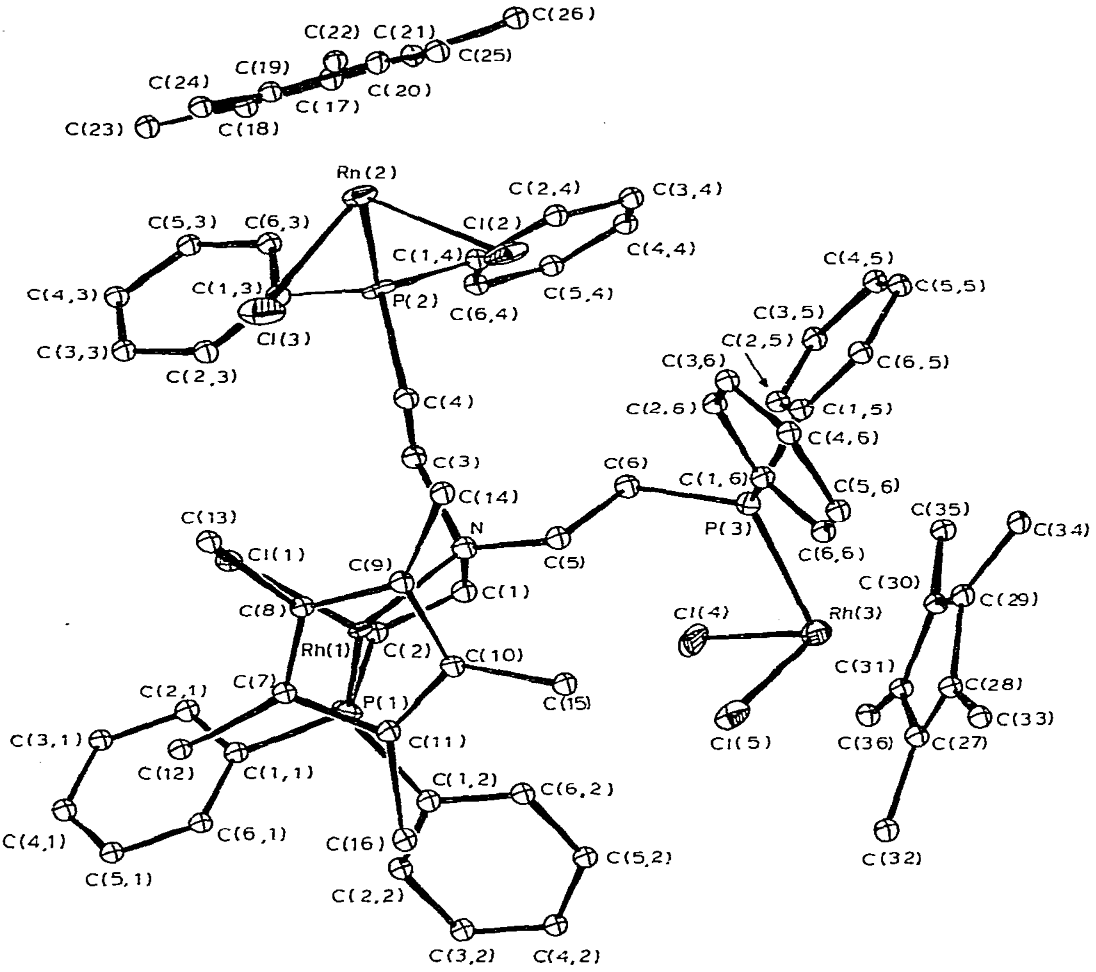

Fig. 1. Perspective view of the $[\{Rh(C_5Me_5)\}Cl_5np_3]^+$ complex cation.

this suggests that these units are not affected by the two neighbouring $Rh(C_5Me_5)$ moieties. The coordination polyhedron of the $\overline{NCH_2CH_2P}Rh(C_5Me_5)$-Cl unit has a rhodium to nitrogen distance (2.39(4) Å) longer than corresponding distances in analogous species [9]; in the present cation this feature is shown by the fact that the rhodium to nitrogen distance is even longer than the Rh—Cl (2.36(2) and the Rh—P 2.30(2) Å) bond lengths. Furthermore, the N—Rh(1)—P(1) and P(1)—Rh(1)—Cl(1) angles are significantly smaller than 90°. Such contractions have been found in complexes with polydentate ligands having small "bite angles" between the two adjacent donor atoms [10], i.e. when two donors give rise to a five-membered ring with the metal.

The Rh(1), Rh(2) and Rh(3) atoms lie 1.82, 1.78 and 1.83 Å, respectively, away from the best plane through the atoms of the carbocyclic rings. Such distances are comparable to those observed in related complexes [4,11]. The C_5

rings of the three pentamethylcyclopentadienyl groups are not coplanar with the Me_5 carbon atoms. The planes through the methyl carbon atoms are 0.2, 0.1 and 0.1 Å further away from the Rh(1), Rh(2) and Rh(3) atoms, respectively, than are the corresponding C_5 rings. These distortions are comparable to those reported for other complexes [3,12]; the largest one refers to the $\overline{NCH_2CH_2PRh}(C_5Me_5)Cl$ unit. The $\overline{NCH_2CH_2PRh}(C_5Me_5)Cl$ unit also shows several other features which are indicative of steric strain about Rh(1). This may be caused by the bulky phenyl groups on the phosphorus atoms and the small bite angle of the P—N donors.

It should be noted that the two $PRh(C_5Me_5)Cl_2$ units are not symmetrically arranged about the plane passing through the N, P and Rh atoms of the $\overline{NCH_2CH_2PRh}(C_5Me_5)Cl$ part of the complex cation. This inequivalence, caused in part by the fact that the ethylenic chain in the above fragment cannot form a planar chelate ring, is likely to exist also in solution, due to the bulkiness of the peripheral $Rh(C_5Me_5)Cl_2PPh_2$ groups, and accounts for the distinct resonances of these groups in the ^{31}P NMR spectra of the compound [4].

Acknowledgment

The authors gratefully acknowledge support of this collaborative effort through a NATO grant.

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