ADVANCES IN INORGANIC CHEMISTRY, VOL. 40

QUADRUPLY BRIDGED DINUCLEAR COMPLEXES OF PLATINUM, PALLADIUM, AND NICKEL

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I. Introduction

Quadruply bridged dinuclear complexes (so-called lantern-type complexes) (Fig. 1) are known for a wide variety of transition metal ions such as Cu, Cr, Mo, W, Tc, Re, Ru, Os, Rh, Ir, Ni, Pd, and Pt, and they appear to be one of the most important common basic structures of transition metal complexes (*1–3*). Most bridging ligands form five-membered rings on bridging between two metal ions. Platinum com-

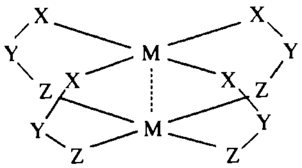

FIG. 1. Basic structure of quadruply bridged dinuclear complexes.

plexes of this type are one of the latest developments and yet have emerged as one of the most versatile with respect to the coordinating atoms of the bridging ligands, including O, N, P, S, and C. The lantern-type platinum complexes are unique compared with those of other metal ions in the sense that both divalent and trivalent complexes as well as mixed valence ones are very often well characterized. The first structurally characterized Pt complex appears to be $K_2[Pt_2(SO_4)_4(H_2O)_2]$ in 1976 (*4*). Major development of the lantern-type diplatinum complexes came after 1980 with the preparation and characterization of the complexes of various type of bridging ligands. Those with pyrophosphite ions (pop[1]) as a bridging ligand, which were first structurally characterized in 1980 (*5*), are by far the most important complexes. Because of their characteristic strong emission, the Pt(II) pop complexes were thoroughly investigated from various viewpoints (*6–8*).

Structural characterization of the lantern-type dipalladium(II) (*9*) and dinickel(II) (*10*) complexes appeared shortly before the report of $K_2[Pt_2(SO_4)_4(H_2O)_2]$. Their chemistry did not develop as much as that of the platinum complexes, however. This is probably because of the limitation of the bridging ligands to give the lantern-type Pd and Ni complexes and also of a lesser trend of these metal ions to give stable complexes with higher oxidation states.

In this review, we will survey the reported results of quadruply bridged diplatinum, dipalladium, and dinickel complexes and discuss their properties from various points of view. Mixed-metal complexes of this type that have been prepared will also be dealt with. We summarize first the known complexes by emphasizing the structural data and the preparation route, and then compare their various properties in as systematic a way as possible.

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[1] Abbreviations used: pop, dianion of pyrophosphite ($P_2O_5H_2^{2-}$); pcp, dianion of μ-methylenebis(phosphite); im, anion of imidazole; 4-mpyt, anion of 4-methylpyridine-2-thiol; pyt, anion of pyridine-2-thiol; pyms, anion of pyrimidine-2-thione; bttz, anion of 1,3-benzothiazole-2-thiol; form, anion of di-*p*-tolylformamidine; dpb, *N*,*N*′-diphenylbenzamidine; mhp, anion of 6-methyl-2-hydroxypyridine; chp, 6-chloro-2-hydroxypyridine; and dpt, 1,3-diphenyltriazen.

Since review articles are available on the Pt pop complexes (*6–8*), we will not describe the pop series of complexes in detail. In particular, extensive studies on their photochemical and photophysical properties will be omitted here, except for the cases in which information is required for comparative purpose. Review articles dealing with Pt(III) dimers (*11*) and linear chain dimer complexes (*12*) have been published.

Before proceeding with more detailed discussion, some characteristic features of the quadruply bridged diplatinum complexes will be pointed out compared with other analogous forms: (i) complexes with a wide variety of ligands are available; these follow the most versatile dimolybdenum(II) complexes (*1*), (ii) for some ligands both divalent and trivalent states are known with no metal–metal bond in the former and a metal–metal single bond in the latter, and (iii) metal–metal distances span a fairly wide range (Pt(III) dimers, 2.39–2.78 Å), the widest among the lantern-type complexes of various metal ions. The last feature is well illustrated in Fig. 2, in which the metal–metal distance is plotted against the bite distance (distance between the coordinated atoms of a bridging ligand) of the ligand for platinum(III) and molybdenum(II) dimers, the latter being representative of other metal complexes. It is clear that the Mo—Mo distances remain almost constant regardless of the bite distance of the bridging ligands. Further discussion on this point will occur later.

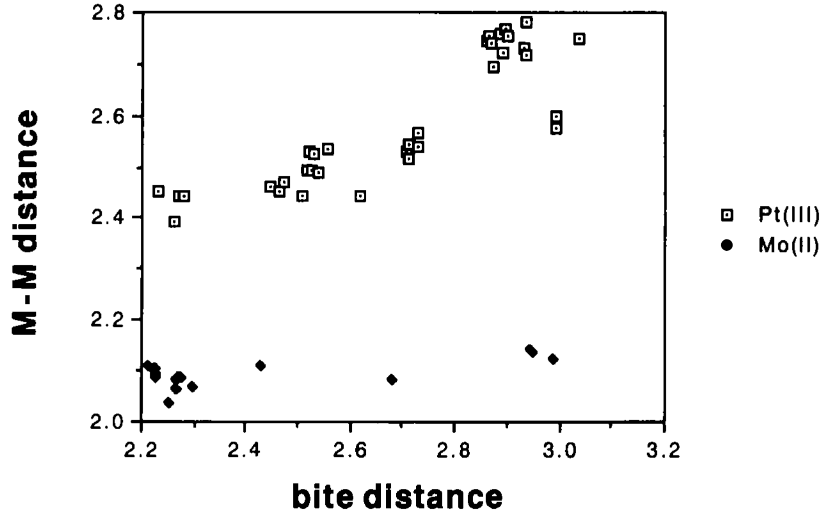

FIG. 2. Correlation diagram of the Pt(III)—Pt(III) distance and the Mo(II)—Mo(II) distance vs the ligand bite distance.

II. Preparation and Steric Structures

Table I summarizes structurally characterized quadruply bridged dinuclear platinum, palladium, and nickel as well as mixed-metal complexes, together with some structural data. Important basic structural characteristics are as follows. The Pt(II) dimers have no axial ligand and each platinum ion has essentially a planar geometry with no metal–metal bonding interaction (Fig. 3a). On the other hand, the Pt(III) dimers usually have axial ligands and each platinum ion has octahedral geometry including the metal–metal single bond (Fig. 3b). The mixed-valence Pt(II)Pt(III) state is known, in which case the number of axial ligands per dimer is 1 (Fig. 3c). The axial ligand usually acts as a bridging ligand, and the dimeric complex becomes an infinite chain structure in the solid state. The two platinum ions in the mixed-valence dimer are considered to be equivalent when halogen atoms centrally bridge the Pt_2(bridging ligand)$_4$ units. The mixed-valence structure is usually unstable in solution. Similar structural characteristics are also seen for the available dipalladium complexes and the PdPt mixed-metal complexes. The nickel(II) ions in carboxylate bridged dinickel(II) complexes and those in the PdNi and PtNi complexes have an axial ligand (see Section II—*1*).

Before further discussion, some technical terms relevant to the structural discussions are described here. Bite distance (*B*) is the distance

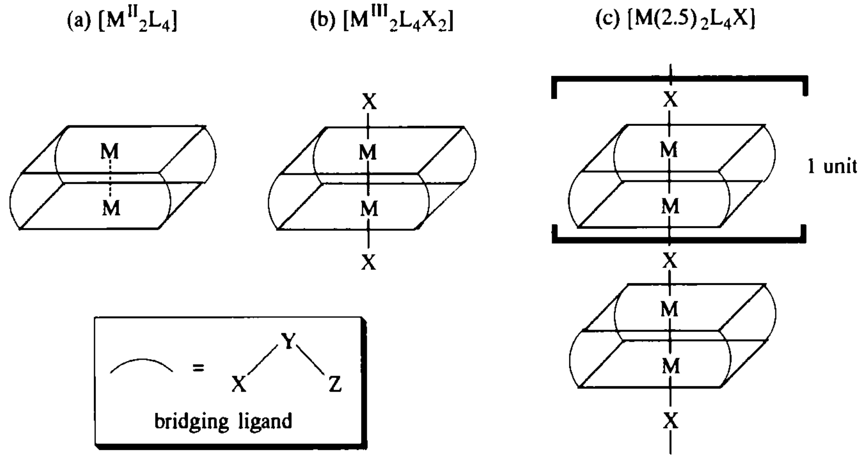
(a) $[M^{II}_2L_4]$ (b) $[M^{III}_2L_4X_2]$ (c) $[M(2.5)_2L_4X]$

FIG. 3. Basic structures of quadruply bridged dinuclear complexes for the oxidation states of +2, +3, and +2.5.

TABLE I

STRUCTURAL DATA FOR QUADRUPLY BRIDGED DIPLATINUM, DIPALLADIUM, AND DINICKEL COMPOUNDS[a]

Compound[b]	Oxidation state	Ligand type[c]	Bite distance[d] (Å)	M—M distance (Å)	Deviation[d,e] (Å)	Twist angle[d] (°)	M—M—X (°)	M—X (Å)	Reference
A. Platinum compounds									
$K_4[Pt_2(pcp)_4]\cdot 6H_2O$	(II, II)	P—P	3.12	2.9801(2)	0.07	0.2	—	—	*55*
$[Pt_2(n\text{-}C_6H_{13}CS_2)_4]$	(II, II)	S—S	3.11	2.855(1)	0.03	27.2	—	—	*37*
$[Pt_2(PhCH_2CS_2)_4]$	(II, II)	S—S	3.04	2.764(1)	0.05	24.9	—	—	*38*
$[Pt_2(CH_3CS_2)_4]$	(II, II)	S—S	3.04	2.767(1)	0.09	20	—	—	*34*
$K_4[Pt_2(pcp)_4Cl_2]\cdot 8H_2O$	(III, III)	P—P	3.04	2.7500(3)	0.14	0.4	176.66(3)	2.442(1)	*55*
$[Pt_2(CH_3CS_2)_4I]$	(II, III)	S—S	3.02	2.677(2)	0.11	21.4	180	2.981(3), 2.975(3)	*35*
$[Pt_2(PhCH_2CS_2)_4I_2]$	(III, III)	S—S	2.99	2.598(2)	0.12	24.0	178.5(2)	2.753(3)	*39*
$[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$	(III, III)	S—S	2.99	2.578(1)	0.11	27	179.75(4), 179.38(5)	2.764(2), 2.763(2)	*39*
$K_4[Pt_2(pop)_4]\cdot 2H_2O$	(II, II)	P—P	2.98	2.925(1)	0.03	0	—	—	*5, 52*
$Ba_2[Pt_2(pop)_4]\cdot 8H_2O$	(II, II)	P—P	2.97	2.949(0)	0.01	0.0	—	—	*54*
$(NH_4)_4[Pt_2(pop)_4Cl]$	(II, III)	P—P	2.95	2.830(1)	0.04	0	180	2.363(4), 3.022(4)	*57*
$K_4[Pt_2(pop)_4Cl]\cdot 2H_2O$	(II, III)	P—P	2.94	2.835(1)	0.05	0.1	175.6(1)	2.406(4), 3.362(4)	*58*
$K_4[Pt_2(pop)_4Br]\cdot 2H_2O$	(II, III)	P—P	2.94	2.834(1)	0.05	0.1	177.31(3)	2.539(1), 3.217(1)	*58*
$K_4[Pt_2(pop)_4Cl]\cdot 3H_2O$	(II, III)	P—P	2.94	2.813(1)	0.06	0	180	2.367(7), 2.966(8)	*56*
$K_4[Pt_2(pop)_4CH_3I]\cdot 2H_2O$	(III, III)	P—P	2.94	2.782(1)	0.08	0	180	2.816(3), 2.18(3)	*8, 107, 131*
$[Bu_4N]_4[Pt_2(pop)_4Br_2]$	(III, III)	P—P	2.94	2.716(1)	0.10	0.3	179.3	2.572(1)	*8, 106, 107*
$K_4[Pt_2(pop)_4Br]\cdot 3H_2O$	(II, III)	P—P	2.93	2.793(1)	0.07	0	180	2.699(1)	*52*
$Na_8[Pt_2(pop)_4(NO_2)_2]\cdot 18H_2O$	(III, III)	P—P	2.93	2.7333(3)	0.06	16.2	179.7(2)	2.153(6)	*8, 132*
$K_4[Pt_2(pop)_4I_2]\cdot 2H_2O$	(III, III)	P—P	2.90	2.754(1)	0.07	0	180	2.746(1)	*8, 106*
$[Bu_4N]_2[Pt_2(pop)_4(SEt_2)_2]$	(III, III)	P—P	2.90	2.766(1)	0.07	0.8	173.4(1)	2.479(5)	*124*
$K_4[Pt_2(pop)_4(SCN)_2]\cdot 2H_2O$	(III, III)	P—P	2.89	2.760(1)	0.06	0.3	172.8(1)	2.466(4)	*8, 107*
$K_4[Pt_2(pop)_4Br_2]\cdot 2H_2O$	(III, III)	P—P	2.89	2.723(4)	0.08	0	180	2.555(5)	*8, 56*
$K_2[Bu_4N]_2[Pt_2(pop)_4I_2]$	(III, III)	P—P	2.87	2.742(1)	0.06	0.3	179.1	2.721(1)	*8, 106*
$K_4[Pt_2(pop)_4Cl_2]\cdot 2H_2O$	(III, III)	P—P	2.87	2.695(1)	0.09	0.1	179.00(5)	2.407(2)	*8, 52, 107*
$K_4[Pt_2(pop)_4(NO_2)_2]\cdot 2KNO_2\cdot 2H_2O$	(III, III)	P—P	2.86	2.754(1)	0.05	0.3	178.7(2)	2.147(6)	*8, 107*
$K_4[Pt_2(pop)_4(im)_2]\cdot 7H_2O$	(III, III)	P—P	2.86	2.745(1)	0.06	0.3	179.1(4)	2.13(2)	*8, 107*
cis-$[Pt_2(4\text{-}mpyt)_4]\cdot C_7H_8$	(II, II)	N—S	2.74	2.680(2)	0.00	13.1	—	—	*47*
trans-$[Pt_2(4\text{-}mpyt)_4]$	(II, II)	N—S	2.73	2.683(3)	−0.02	17.1	—	—	*104*
cis-$[Pt_2(pyt)_4(CN)_2]\cdot 2CHCl_3$	(III, III)	N—S	2.73	2.566(2)	0.00	23.4	173.6(3)	2.09(1)	*104*
trans-$[Pt_2(4\text{-}mpyt)_4I_2]\cdot 3C_6H_6$	(III, III)	N—S	2.73	2.539(1)	−0.06	32.0	180	2.780(2), 2.788(2)	*104*
3S1N-$[Pt_2(pymS)_4Cl_2]$	(III, III)	N—S	2.71	2.518(1)	−0.03	29.0	178.7(1), 179.7(1)	2.440(3), 2.463(3)	*45*
$[Pt_2(2\text{-}thiouracilato)_4I_2]$	(III, III)	N—S	2.71	2.546(2)	0.00	25.3	170.2(1), 172.5(1)	2.776(4), 2.766(3)	*45*

Continued

TABLE I—*continued*

Compound^b	Oxidation state	Ligand type^c	Bite distance^d (Å)	M—M distance (Å)	Deviation^{d,e} (Å)	Twist angle^d (°)	M—M—X (°)	M—X (Å)	Reference
cis-$[Pt_2(pyt)_4Cl_2]\cdot 2CHCl_3$	(III, III)	N—S	2.71	2.532(1)	0.01	23.3	172.6(1)	2.458(2)	*47*
$Na_{10}[Pt_2(PO_4)_4(C_5H_3N_5O)_2]\cdot 22H_2O$	(III, III)	O—O	2.56	2.5342(4)	0.01	0.3	177.32(6)	2.141(2)	*21*
$Na_2[Pt_2(HPO_4)_4(H_2O)_2]$	(III, III)	O—O	2.54	2.487(2)	0.03	0.2	177.5(3), 178.2(3)	2.161(13), 2.140(13)	*15, 133*
$[Ph_4As]_2[Pt_2(HPO_4)_4(S(CH_2)_4)_2]\cdot 2H_3PO_4$	(III, III)	O—O	2.53	2.525(1)	0.00	1.3	178.74(3)	2.462(1)	*18*
$(C_7H_{10}N)_2[Pt_2(HPO_4)_4(C_7H_9N)_2]$	(III, III)	O—O	2.53	2.494(1)	0.02	0.5	179.1(3)	2.164(11)	*20*
$[Et_4N]_2[Pt_2(H_2PO_4)_2(HPO_4)_2Cl_2]\cdot H_2O$	(III, III)	O—O	2.52	2.529(1)	0.00	1.3	179.7(1)	2.448(4)	*15*
$(pyH)[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]\cdot H_2O$	(III, III)	O—O	2.52	2.494(1)	0.01	13.3	176.9(4), 178.1(4)	2.179(13), 2.11(2)	*19*
$K_2[Pt_2(SO_4)_4(OSMe_2)_2]\cdot 4H_2O$	(III, III)	O—O	2.47	2.471(1)	0.00	0.3	177.0(2)	2.126(6)	*16*
$K_2[Pt_2(SO_4)_4(H_2O)_2]$	(III, III)	O—O	2.45	2.461(1)	−0.01	0.5	179.4(3)	2.111(7)	*15*
$K[Pt_2(CH_3CO_2)_3(CH_2CO_2)Cl_2]\cdot 1.5H_2O$	(III, III)	O—O; O—C	2.28, 2.62	2.442(3)	−0.04	3.7	177.5(4), 175.5(4)	2.46(2), 2.43(2)	*25*
$[Pt_2(CH_3CO_2)_3(CH_2CO_2)Cl(py)]$	(III, III)	O—O; O—C	2.27, 2.51	2.445(1)	−0.06	1.9	178.2(2)^f, 178.7(5)^g	2.403(6)^h, 2.19(2)^i	*25*
$Cs_3[Pt_2(CH_3CO_2)_2(CH_2CO_2)_2Cl_2]Cl\cdot 3H_2O$	(III, III)	O—O; O—C	2.23, 2.47	2.451(1)	−0.05	4.8	175.4(2), 177.5(2)	2.46(1), 2.42(1)	*24*
$[Pt_2(CH_3CO_2)_4(H_2O)_2](ClO_4)_2$	(III, III)	O—O	2.26	2.3905(14)	−0.06	0.6	178.0(3)	2.167(12)	*30, 31*
$[Bu_4N]_2[Pt_2(pop)_4(CH_3CN)_2]$	(III, III)	P—P	—^{j}	2.676(1)	—^{j}	—^{j}	—^{j}	2.093(10)	*134*
cis-$[Pt_2(pymS)_4I_2]$	(III, III)	N—S	—^{j}	2.554(1)	—^{j}	26	173.8(1), 172.6(1)	2.768(2), 2.779(2)	*44*
cis-$[Pt_2(pymS)_5Cl]$	(III, III)	N—S	—^{j}	2.547(2)	—^{j}	—^{j}	175.8(2), 172.8(2)	2.494(7), 2.438(8)	*46*
B. Palladium compounds									
$[Pd_2(CH_3CS_2)_4]\cdot CS_2$ (form B)	(II, II)	S—S	3.02	2.738(1)	0.06	24.0	—	—	*74*
$[Pd_2(PhCH_2CS_2)_4]$	(II, II)	S—S	3.02	2.715(3)	0.06	25.4	—	—	*75*
$[Pd_2(bttz)_4]$	(II, II)	N—S	2.75	2.745(1)	−0.01	1.1	—	—	*76*
$[Pd_2(pyt)_4]\cdot 2CHCl_3$	(II, II)	N—S	2.73	2.677(1)	0.03	1.5	—	—	*84*
$[Pd_2(pyt)_4Cl_2]\cdot 2CHCl_3$	(III, III)	N—S	2.72	2.528(1)	0.01	0.3	171.5(1)	2.452(2)	*104*
$[Pd_2(form)_4]PF_6$	(II, II)	N—N	2.40	2.637(6)	−0.16	17	—	—	*79*
$[Pd_2(mhp)_4]$	(II, II)	N—O	2.34	2.546(1)	−0.11	6.4	—	—	*81*
$[Pd_2(form)_4]\cdot 2H_2O$	(II, II)	N—N	2.33	2.622(3)	−0.18	15.1	—	—	*79*
$[Pd_2(chp)_4]$	(II, II)	N—O	2.33	2.563(1)	−0.12	6	—	—	*82*
$[Pd_2(dpb)_4]\cdot EtOH$	(II, II)	N—N	2.32	2.576(1)	−0.16	14.1	—	—	*80*
$[Pd_2(dpt)_4]$	(II, II)	N—N	2.23	2.5626(7)	−0.18	13	—	—	*9*
C. Nickel compounds									
$[Ni_2(PhCH_2CS_2)_4]$	(II, II)	S—S	3.00	2.551(3)	0.13	28.5	—	—	*75*
$[Ni_2(CH_3CS_2)_4]$	(II, II)	S—S	2.99	2.564(1)	0.12	27.5	—	—	*86*
$[Ni_2(CH_3CS_2)_4I]$	(II, III)	S—S	2.97	2.514(5)	0.12	28.8	180	2.928(4), 2.940(4)	*86*
$[Ni_2(SOCPh)_4(EtOH)]$	(II, II)	S—O	2.61	2.503(4)	0	23.4	—	2.058(7)^k	*92*

$[Ni_2(form)_4]BF_4$	(II, III)	N—N	2.34	2.418(4)	−0.13	27.4	—	—	*79*
$[Ni_2(form)_4]\cdot 2H_2O$	(II, II)	N—N	2.34	2.485(2)	−0.11	16.8	—	—	*79*
$[Ni_2(dpt)_4]$	(II, II)	N—N	2.23	2.395(3)	−0.12	16	—	—	*9*
$[Ni_2(MePh_2CCOO)_4(quinoline)_2]\cdot 2CHCl_3$	(II, II)	O—O	2.23	2.765(1)	−0.27	3.8	165.0(2)	2.024(6)	*97*
$[Ni_2(Me_2PhCCOO)_4(quinoline)_2]$	(II, II)	O—O	2.23	2.7337(7)	−0.26	2.1	165.70(9)	2.040(3)	*97*
$[Ni_2(MePh_2SiCOO)_4(Ph_3P)_2]$	(II, II)	O—O	2.23	2.7079(8)	−0.24	0.5	166.66(5)	2.368(1)	*97*
$[Ni_2(Me_3CCOO)_4$(2,5-lutidine)$_2]$	(II, II)	O—O	2.22	2.7202(8)	−0.25	1.8	160.8(1)	2.034(3)	*97*
$[Ni_2(Me_3CCOO)_4$(2-ethylpyridine)$_2]$	(II, II)	O—O	2.21	2.7227(7)	−0.26	0.6	166.00(6)	2.042(3)	*97*
$[Ni_2(Me_3CCOO)_4$(2-picoline)$_2]$	(II, II)	O—O	2.21	2.7171(7)	−0.26	1.9	169.47(7)	2.037(3)	*97*
$[Ni_2(Me_3CCOO)_4$(2,4-lutidine)$_2]$	(II, II)	O—O	2.21	2.7080(5)	−0.25	0.3	166.63(5)	2.035(2)	*96*
$[Ni_2(Me_3CCOO)_4(quinaldine)_2]$	(II, II)	O—O	—[j]	2.754(3)	—[j]	—[j]	—[j]	2.07(1)	*95*
D. Mixed-metal compounds									
$[PtPd(4\text{-}mpyt)_4]_{0.67}[Pd_2(4\text{-}mpyt)_4]_{0.33}\cdot CH_2Cl_2$	(II, II)	N—S	2.74	2.673(1)[l]	0.03	1.8	—	—	*104*
$[PdNi(4\text{-}mpyt)_4(MeCN)]\cdot MeCN$	(II, II)	N—S	2.71	2.541[m]	−0.03[n], −0.07[o]	29.9[m]	—	2.12(2)[k,m]	*103*
$[PtPd(5\text{-}mpyt)_4Cl_2]$	(III, III)	N—S	2.71	2.568(1)	0.07	1.6	167.5	2.482(2)	*104*
$[PtNi(4\text{-}mpyt)_4(MeCN)]\cdot MeCN$	(II, II)	N—S	2.70	2.539[m]	−0.02[p], −0.08[o]	29.1[m]	—	2.13(2)[k,m]	*102*

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[a] The data listed in the table are calculated from the atomic coordinates when the corresponding data are missing in the literature.

[b] Ligand abbreviations are as follows: pop, dianion of pyrophosphite ($P_2O_5H_2^{2-}$); pcp, dianion of μ-methylenebis(phosphite); im, anion of imidazole; 4-mpyt, anion of 4-methylpyridine-2-thiol; pyt, anion of pyridine-2-thiol; pymS, anion of pyrimidine-2-thione; bttz, anion of 1,3-benzothiazole-2-thiol; form, anion of di-*p*-tolylformamidine; dpb, *N*,*N*′-diphenylbenzamidine; mhp, anion of 6-methyl-2-hydroxypyridine; chp, 6-chloro-2-hydroxypyridine; dpt, 1,3-diphenyltriazen.

[c] Ligand type indicates the coordinating atoms of the bridging ligands.

[d] The mean value.

[e] The deviation of each metal atom from the coordintion plane defined by the four donor atoms.

[f] The Pt—Pt—Cl angle.

[g] The Pt—Pt—N angle.

[h] The Pt—Cl distance.

[i] The Pt—N distance.

[j] This value could not be calculated owing to lack of atomic coordinates in the literature.

[k] The Ni—X distance.

[l] The mean value of Pt—Pd and Pd—Pd distances.

[m] The mean value between two independent molecules.

[n] The deviation for the Pd atom.

[o] The deviation for the Ni atom.

[p] The deviation for the Pt atom.

between the two coordinating atoms within a ligand as determined by X-ray structural analysis (Fig. 4a). The bite distance may be slightly different among different complexes with the same ligand. Deviations (δ) of each metal atom from the coordination plane defined by the four donor atoms are taken as a plus value when the metal atoms deviate from the coordination plane toward each other. It directly correlates with the difference between the bite and the metal–metal distances only when the complexes have an eclipsed configuration. Most complexes have structures that deviate from an ideal eclipsed configuration. The extent of the deviation is represented by the twist angle, which is defined by the dihedral angle X—M—M—Z (Fig. 4b).

A. PLATINUM DIMERS WITH SULFATE AND PHOSPHATE AS BRIDGING LIGANDS (O—O)

Among the bridging ligands with the shortest bite distance are the oxygen-donor anions sulfate, phosphate (in the form of hydrogen and dihydrogen phosphate in the known quadruply bridged diplatinum complexes), and acetate. The acetate complexes will be discussed in the next section.

The sulfate and phosphate complexes have been prepared by heating Pt(II) nitro complexes, $K_2[Pt(NO_2)_4]$ (*13*) and $[Pt(NH_3)_2(NO_2)_2]$ (*14*), respectively, in the corresponding concentrated acid.

$$[Pt(NO_2)_4]^{2-} \xrightarrow[\Delta]{H_2SO_4} [Pt_2(SO_4)_4(OH)(H_2O)]^{3-} \longrightarrow [Pt_2(SO_4)_4(H_2O)_2]^{2-}$$

$$cis\text{- or } trans\text{-}Pt(NH_3)_2(NO_2)_2 \xrightarrow[\Delta]{H_3PO_4} (NH_4)_2[Pt_2(HPO_4)_4(H_2O)_2]$$

Axially substituted derivatives of sulfate bridged dimers, $M_4[Pt_2(SO_4)_4X_2]$, $M_4[Pt_2(SO_4)_4XY]$, and $M_2[Pt_2(SO_4)_4L_2]$ ($M^+ = K^+, Cs^+, NH_4^+; X^-, Y^- = OH^-, H_2O, Cl^-, Br^-, NO_2^-; L = H_2O, NH_3, Me_2SO$) are obtained by substitution of the axial ligands of $[Pt_2(SO_4)_4(OH)(H_2O)]^{3-}$ by X^-, Y^-, or L ligands (*4, 13, 15–17*).

$$\begin{aligned}
&[Pt_2(SO_4)_4(OH)(H_2O)]^{3-} + KX, NH_4OH, \text{or } L\\
&\qquad \longrightarrow [Pt_2(SO_4)_4X_2]^{4-} (X = OH, Cl, Br, SCN, NO_2),\\
&\qquad\qquad [Pt_2(SO_4)_4L_2]^{2-} (L = NH_3, MeNH_2, Me_2SO),\\
&\qquad\qquad \text{or } [Pt_2(SO_4)_4(OH)X]^{4-} (X = Cl, NO_2)
\end{aligned}$$

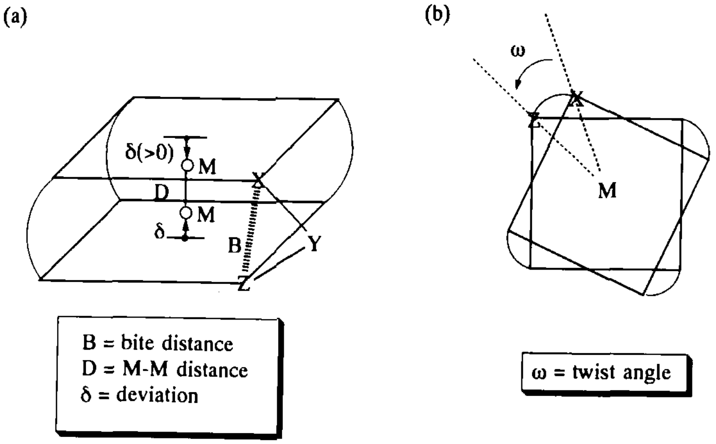


FIG. 4. Technical terms used in the structural discussion.

The axial ligands of $(NH_4)_2[Pt_2(HPO_4)_4(H_2O)_2]$ can also be substituted by halide (*15, 18*), pyridine (*19, 20*), guanine (*21*), and various amines, thioethers, and thiolates (*18*).

Two sulfate and six phosphate complexes with various axial ligands have been structurally characterized. The X-ray structure of $K_2[Pt_2(SO_4)_4(H_2O)_2]$ was first reported by Muraveiskaya *et al.* (*4*) and was redetermined by Bancroft *et al.* (*15*) (Fig. 5). The Pt—Pt distance in the former determination was 2.466 Å. The Me_2SO complex, $[Pt_2(SO_4)_4(Me_2SO)_2]^{2-}$, has a slightly longer Pt—Pt distance (2.471(1) Å). The Pt—Pt distances of the six phosphate (HPO_4^{2-} or $H_2PO_4^-$) complexes with different axial ligands are in the narrow range (2.487–2.534 Å). The twist angle is less than 1.3°, except in the case of $[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]^-$, which has a twist angle of 13.3°. The fact that only the Pt(III) dimers have been isolated for sulfate and phosphate bridged complexes indicates that the short bite distance of these ligands destabilizes the $Pt(II)_2$ state, which requires a much longer Pt ··· Pt distance.

B. PLATINUM DIMERS WITH ACETATES AS BRIDGING LIGANDS (O—O AND C—O)

The acetate ion is the most common bridging ligand to form lantern-type complexes, and tetraacetate complexes have been known for some time for all the metal ions that afford this structure except the group

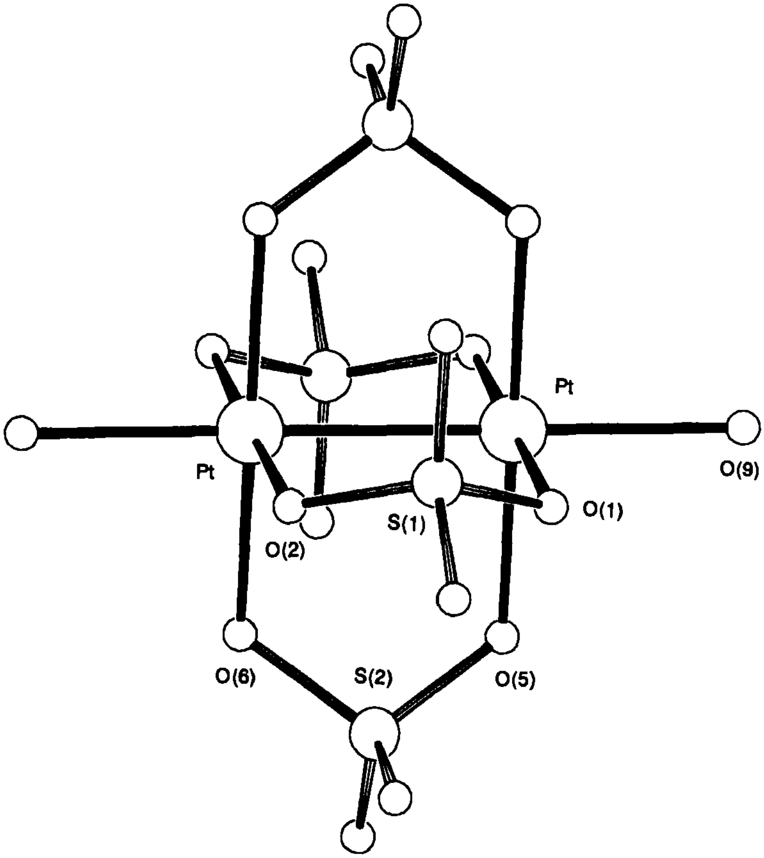


FIG. 5. ORTEP diagram of $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$.

10 elements and iridium. The tetra(acetato)diplatinum(III) complex and trifluoroacetate derivative were described previously without firm evidence for the structure (*22, 23*). In 1990, a complex was isolated from a platinum(II)–acetate reaction mixture, with the unusual structure $[Pt_2(\mu\text{-}CH_2COO\text{-}C,O)_2(\mu\text{-}CH_3COO\text{-}O,O')_2Cl_2]^{2-}$ (Fig. 6), as disclosed by X-ray structural analysis (*24*). The complex has two carbon-bonded CH_2COO^{2-} ligands that are mutually in *cis* positions, each Pt(III) ion taking one Pt—C bond in the X-ray structural analysis. ^1H and ^{13}C NMR spectra supported the view that this structure is retained in solution.

$$[PtCl_4]^{2-} + CH_3COOAg \xrightarrow[\Delta]{CH_3COOH\text{-}H_2O}$$

$$\xrightarrow{HCl} [Pt^{III}{}_2(\mu\text{-}CH_2COO\text{-}C,O)_2(\mu\text{-}CH_3COO\text{-}O,O')_2Cl_2]^{2-}$$

Subsequently, a complex with three normal acetate bridges and one C,O-bonded CH_2COO bridge, $[Pt_2(CH_3COO)_3(CH_2COO)Cl_2]^-$, was isolated from a similar reaction mixture (*25*). Axial ligand substitution of $[Pt_2(CH_3COO)_3(CH_2COO)Cl_2]^-$ in solution gives rise to various derivatives. Thus X-ray structural analysis of $[Pt_2(CH_3COO\text{-}O,O')_3(CH_2COO\text{-}C,O)Cl(py)]$ discloses that the axial Cl^- ligand at the Pt atom

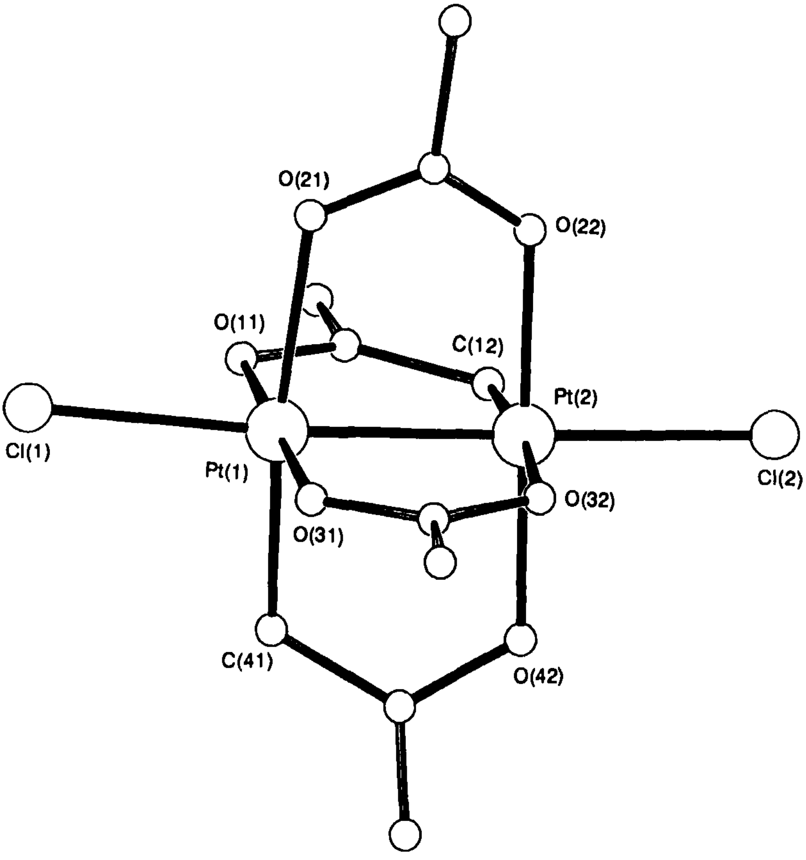
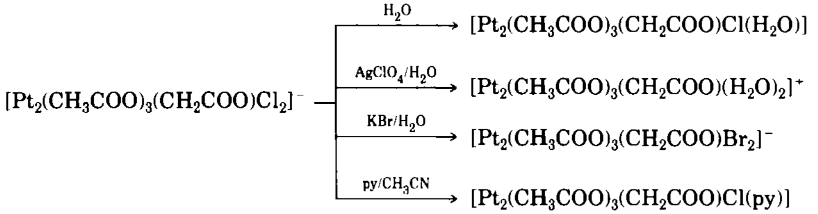


FIG. 6. ORTEP diagram of $[Pt_2(CH_3CO_2)_2(CH_2CO_2)_2Cl_2]^{2-}$.

without a Pt—C bond in the parent dichloro complex is selectively substituted by pyridine (Fig. 7).



$$[Pt_2(CH_3COO)_3(CH_2COO)Cl_2]^- \xrightarrow{H_2O} [Pt_2(CH_3COO)_3(CH_2COO)Cl(H_2O)]$$

$$[Pt_2(CH_3COO)_3(CH_2COO)Cl_2]^- \xrightarrow{AgClO_4/H_2O} [Pt_2(CH_3COO)_3(CH_2COO)(H_2O)_2]^+$$

$$[Pt_2(CH_3COO)_3(CH_2COO)Cl_2]^- \xrightarrow{KBr/H_2O} [Pt_2(CH_3COO)_3(CH_2COO)Br_2]^-$$

$$[Pt_2(CH_3COO)_3(CH_2COO)Cl_2]^- \xrightarrow{py/CH_3CN} [Pt_2(CH_3COO)_3(CH_2COO)Cl(py)]$$

Preparation of carbon-bonded CH_2COO^{2-} complexes gives the impression that the platinum ion favors carbon-bonded structures as is known in the case of various mononuclear platinum complexes (*26–29*), and the tetraacetate complexes do not exist as stable compounds. The tetra(acetato)diplatinum complex, $[Pt_2(CH_3COO)_4(H_2O)_2]^{2+}$ (Fig. 8), was eventually prepared, however, by refluxing a solution of $K_2[Pt(NO_2)_4]$ in CH_3COOH–1 *M* $HClO_4$ (2:1) (*30, 31*).

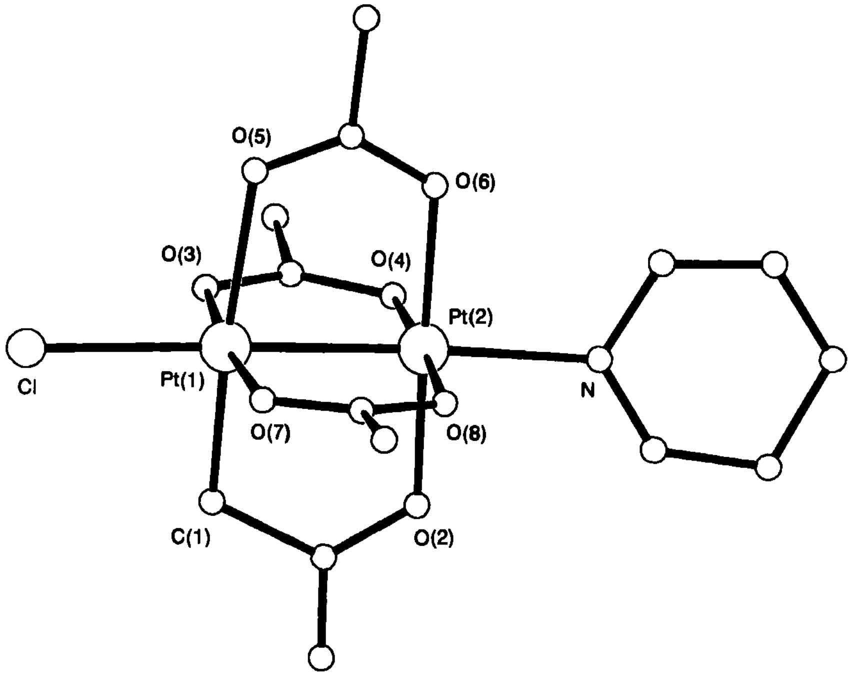


FIG. 7. ORTEP diagram of $[Pt_2(CH_3CO_2)_3(CH_2CO_2)Cl(py)]$.

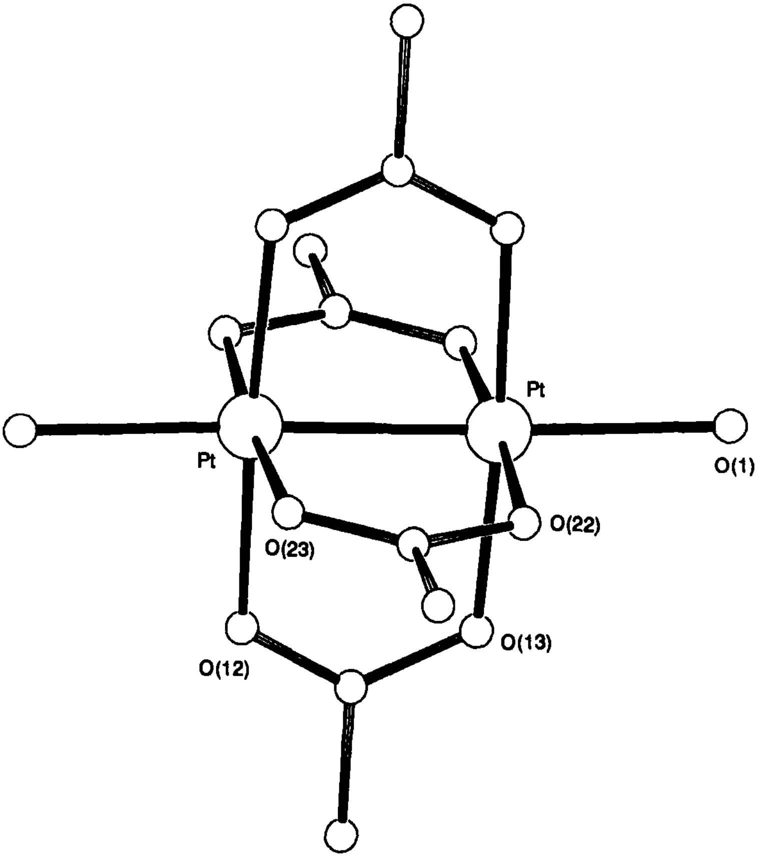


FIG. 8. ORTEP diagram of $[Pt_2(CH_3CO_2)_4(H_2O)_2]^{2+}$.

$$[Pt(NO_2)_4]^{2-} \xrightarrow[\text{AcOH/1}M\text{-HClO}_4]{} [Pt_2(CH_3CO_2)_4(H_2O)_2]^{2+}$$

The tetra(acetato) complex, $[Pt_2(CH_3COO)_4(H_2O)_2]^{2+}$, is unstable in aqueous solution and is unable to release one of the bridging acetate ligands rapidly. It appears, therefore, that previous attempts to obtain evidence for the tetra(acetato) structure in solution failed because of its instability. The tetra(acetato) complex has the shortest Pt—Pt distance so far detected (2.3905(14) Å). The Pt—Pt distances of the carbon-bonded complexes $K[Pt_2(CH_3COO\text{-}O,O')_3(CH_2COO\text{-}C,O)Cl_2]$ and $[Pt_2(CH_3COO\text{-}O,O')_3(CH_2COO\text{-}C,O)Cl(py)]$ are 2.442(3) and 2.445(1) Å, respectively. The Pt—Cl distance at the Pt ion with the carbon donor atom is shorter (2.43(2) Å) than that with the other Pt atom (2.46(2) Å). A complex with two CH_2COO bridges, $[Pt_2(CH_3COO\text{-}O,O')_2(CH_2COO\text{-}C,O)_2Cl_2]$, has a Pt—Pt distance of 2.451(1) Å.

The extremely short bite distance of the acetate ligand forces the complexes to take a short Pt—Pt distance. In fact, the platinum atom deviates from the PtO_4 plane toward the axial ligand (negative δ values). Thus the tetra(acetato) structure should be highly strained, which may be the reason for the observed instability in solution. It is seen that as the number of CH_2COO^{2-} ligands increases, the Pt—Pt distance becomes greater with less strain. In all these complexes, the twist angles were found to be small. With these ligands, no Pt(II) dimer has been prepared, probably because of short ligand bite distances. A number of *cis*-bis(carboxylato) diplatinum complexes such as $[Pt_2(CH_3)_4(CH_3CO_2)_2(py)_2]$ (*26*) and $[Pt_2(CH_3)_4(CF_3CO_2)_2(4\text{-methylpyridine})_2]$ (*32*) are known. Bis(μ-sulfoacetato)diplatinum(II) complexes have also been reported (*33*). In these complexes, the strain is released by a much longer Pt—Pt distance.

C. PLATINUM DIMERS WITH DITHIOCARBOXYLATES AS BRIDGING LIGANDS (S—S)

Quadruply bridged diplatinum complexes with dithiocarboxylates, RCS_2^-, as bridging ligands are known for both Pt(II) and Pt(III) states. The Pt(II) complex, $[Pt_2(CH_3CS_2)_4]$, was prepared by the reaction of $K_2[PtCl_4]$ with dithioacetic acid in hot toluene (*34*). The Pt(II) dimer was reacted with halogen (X_2) to give a corresponding Pt(III) dimer, $[Pt_2(CH_3CS_2)_4X_2]$ (*35*). The Pt(II)Pt(III) mixed-valence complex, $[Pt_2(CH_3CS_2)_4I]$ (Fig. 9), was also prepared by reacting the Pt(II) dimer with half-equivalent amount of iodine or was isolated from the 1:1 mixture of $[Pt_2(CH_3CS_2)_4]$ and $[Pt_2(CH_3CS_2)_4I_2]$. In this case, the crystal structure consists of infinite chains of $\cdots Pt_2(CH_3CS_2)_4 \cdots I \cdots Pt_2(CH_3CS_2)_4 \cdots I \cdots$, lying along the twofold axis of the unit cell, and all the Pt atoms are equivalent. Vibrational spectra of these complexes have also been discussed (*36*).

$$[PtCl_4]^{2-} + 2CH_3CS_2H \xrightarrow[\text{toluene}/\Delta]{} [Pt_2(CH_3CS_2)_4] \xrightarrow{X_2} [Pt_2(CH_3CS_2)_4X_2]$$

$$[Pt_2(CH_3CS_2)_4] + (1/2)I_2 \longrightarrow [Pt_2(CH_3CS_2)_4I]$$

$$[Pt_2(CH_3CS_2)_4] + [Pt_2(CH_3CS_2)_4I_2] \longrightarrow [Pt_2(CH_3CS_2)_4I]$$

Complexes with other dithiocarboxylates such as $n\text{-}C_6H_{13}CS_2^-$ (Fig. 10) (*37*), $PhCH_2CS_2^-$ (*38,39*), and $Me_2CHCS_2^-$ (*38–40*) have been reported.

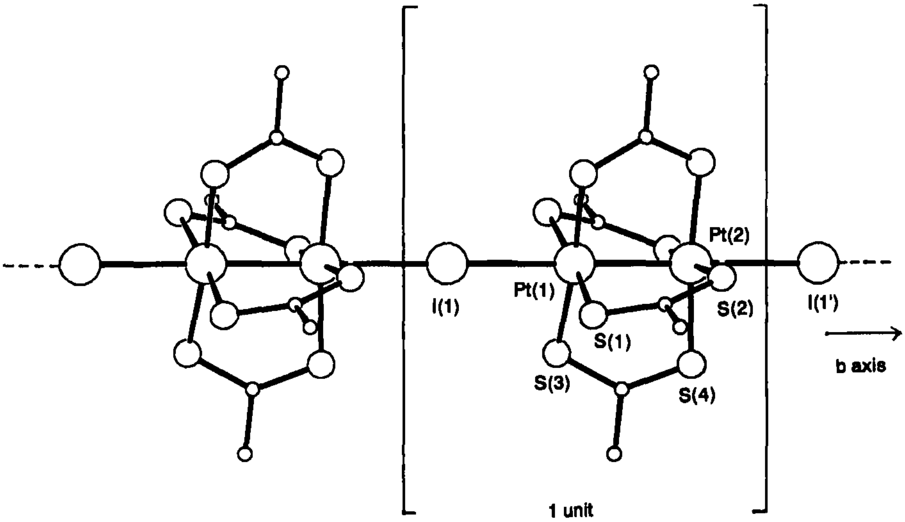


FIG. 9. ORTEP diagram of $[Pt_2(CH_3CS_2)_4I]$.

Some of these complexes have been structurally characterized, and the structural data on all the three different oxidation states are available (Table I). A significant feature is the twist of the two platinum coordination planes defined by the four sulfur atoms. Such a phenomenon is seen for all the oxidation states. The twist angle is as much as 27.2° (*37*). The bite distances observed for these ligands are the largest of those listed in Table I. The twist is the result of adjusting the Pt—Pt distance to a value shorter than the bite distance.

It is interesting that the Pt—Pt distance is significantly shorter than the ligand bite distance even in the Pt(II) dimer, where no direct Pt—Pt interaction is formally expected. This fact is recognized as a manifestation of the d^8–d^8 metal–metal bonding as has been proposed in the case of $[Rh(RNC)_4]_2^{2+}$ (*41–43*). The dominant intramolecular Pt—Pt bonding interaction would arise from valence-shell *d–p* mixing in Pt—Pt σ-type orbitals (*37*). The MO approach has been considered for not only intra- but also intermolecular Pt—Pt interactions. It has been suggested that a short intermolecular Pt—Pt distance would induce the decrease of the intramolecular Pt—Pt distance. Experiments in solution are limited by the low solubility of dithiocarboxylate complexes, which are not usually sufficiently soluble for an investigation of their properties in solution. The n-$C_6H_{13}CS_2^-$ derivative has high solubility, however, toward hydrocarbon, haloalkane, and ethereal solvents (*37*). The solution of $[Pt_2(n\text{-}C_6H_{13}CS_2)_4]$ indicates dimerization and further oligomerization of the dinuclear unit at low temperature.

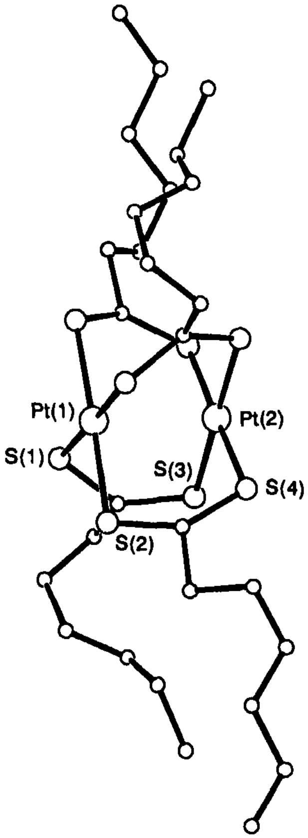
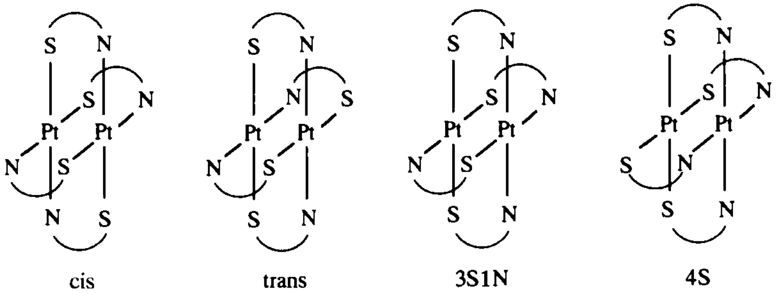


FIG. 10. ORTEP diagram of $[Pt_2(n\text{-}C_6H_{13}CS_2)_4]$.

D. PLATINUM DIMERS WITH PYRIMIDINETHIONATE, PYRIDINETHIOLATE, AND RELATED LIGANDS AS BRIDGING LIGANDS (N—S)

Three kinds of (N–S) bridging ligands are known for the quadruply bridged complexes, namely, pyrimidine-2-thionate (pymS) (*44–46*), 2-thiouracilate (*45*), and pyridine-2-thiolate (pyt) and its 4-methyl derivative (4-mpyt) (*47*). Among these complexes, only the pyridinethiolate complexes have been extensively studied.

When two coordinating atoms of the bridging ligands are different, as in the case of these N–S ligands, four geometrical isomers are possible for the quadruply bridged complexes. Here we call such isomers *cis, trans, 3S1N,* and *4S* isomers according to their structures, as illustrated in Scheme 1.



SCHEME 1

The complexes of pymS and 2-thiouracilate were prepared by the reaction of $K_2[PtX_4]$ ($X^- = Cl^-, Br^-, I^-$) with the bridging ligands (L) in ethanol (or methanol) upon heating. The procedure finally gives the Pt(III) dimer, $[Pt_2(L)_4X_2]$ (*44, 45*). The X-ray structure of *3S1N*-$[Pt_2(pymS)_4Cl_2]$ is shown in Fig. 11.

$$[PtX_4]^{2-} + L \xrightarrow[\text{EtOH or MeOH}]{} \text{(yellow product)} \longrightarrow [Pt_2(L)_4X_2]$$

L = pyrimidine-2-thione,2-thiouracil

The Pt(II) dimer of pyridine-2-thiolate was prepared by refluxing a mixture of *cis*-$[PtCl_2(NH_3)_2]$ and pytH in dioxane for 12 hr. The Pt(II) dimer, *cis*-$[Pt_2(pyt)_4]$, was then reacted with $CHCl_3$, $CHBr_3$, or CH_3I to give the corresponding Pt(III) complexes, *cis*-$[Pt_2(pyt)_4X_2]$ ($X^- = Cl^-, Br^-, I^-$) (*47*).

$$\textit{cis}\text{-}[PtCl_2(NH_3)_2] + 2pytH \xrightarrow[\Delta]{\text{dioxane}} [Pt_2(pyt)_4] \xrightarrow[CHCl_3]{} [Pt_2(pyt)_4Cl_2]$$

The axial ligand (X^-) of $[Pt_2(pyt)_4X_2]$ can be substituted by addition of excess amounts of the halide ion to a solution of $[Pt_2(pyt)_4X_2]$. The mpyt complexes were prepared similarly (*48*).

$$\begin{tikzcd}
 & {[Pt_2(pyt)_4]} \arrow[dl, "CHBr_3"'] \arrow[d, "CHCl_3"] \arrow[dr, "CH_3I"] & \\
{[Pt_2(pyt)_4Br_2]} \arrow[r, shift left, "LiCl"] & {[Pt_2(pyt)_4Cl_2]} \arrow[l, shift left, "NaBr"] \arrow[r, shift left, "NaI"] \arrow[d, "NaSCN"] & {[Pt_2(pyt)_4I_2]} \arrow[l, shift left, "LiCl"] \\
 & {[Pt_2(pyt)_4(SCN)_2]} &
\end{tikzcd}$$

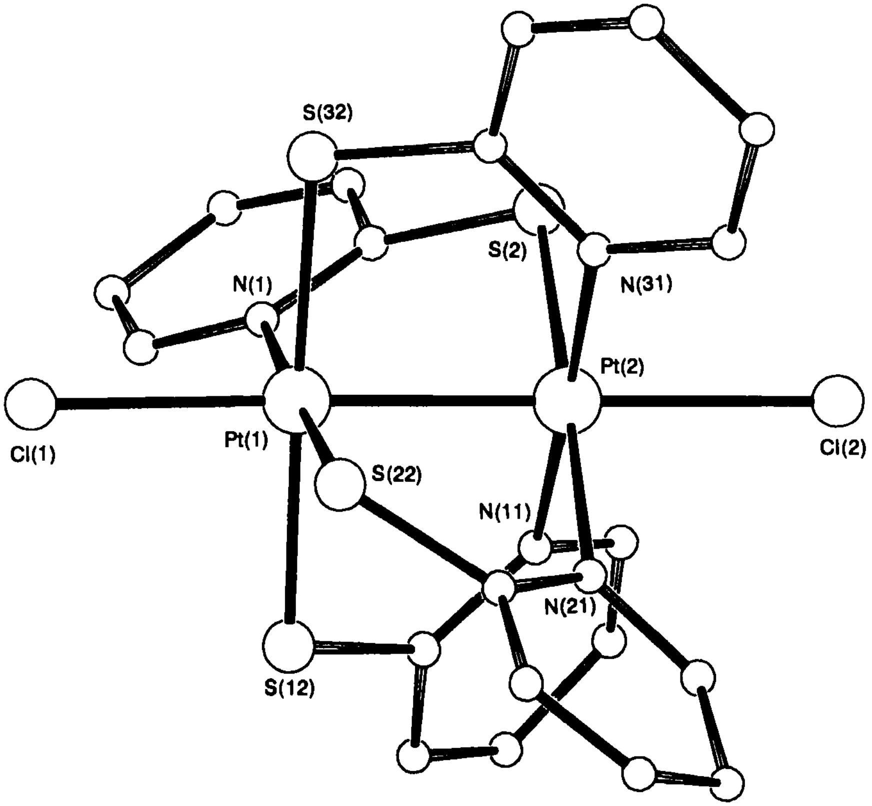


FIG. 11. ORTEP diagram of *3S1N*-[$Pt_2(pymS)_4Cl_2$].

The reaction of pytH with *cis*-[$PtCl_2(NH_3)_2$] selectively gives the *cis*-isomer. In the case of 4-mpytH, however, a mixture of geometrical isomers, *cis, trans,* and *3S1N,* is obtained, although the preparation procedures are similar (*48*). Exclusive formation of the *cis*-isomer for pyt is probably due to low solubility of [$Pt_2(pyt)_4$] toward the reaction solvent, dioxane. Whereas the *cis*-isomers of [$Pt_2(pyt)_4$] and [Pt_2(4-mpyt)$_4$] abstract Cl from $CHCl_3$ to give corresponding Pt(III) dimers, the *trans*-isomer of [Pt_2(4-mpyt)$_4$] is stable in $CHCl_3$ and requires halogen oxidation to obtain the Pt(III) states.

The X-ray structures of *cis*-[Pt_2(4-mpyt)$_4$] and *cis*-[$Pt_2(pyt)_4Cl_2$] are shown in Fig. 12 and Fig. 13, respectively. The Pt ··· Pt distance of the former is 2.680(2) Å, which is the shortest Pt ··· Pt distance in the structurally characterized Pt(II) dimers, and that of the latter is 2.532(1) Å. The two coordination planes in each compound twist toward each other along the Pt—Pt axis; the average torsion angles in *cis*-[Pt_2(4-mpyt)$_4$] and *cis*-[Pt_2(pyt)$_4Cl_2$] are 13.1° and 23.3°, respectively. The increase of the torsion angle should be due to the requirement for a shorter Pt—Pt distance for the latter. A more detailed discussion will be given later (Section II–J). The *trans*- and the *cis*-isomers of [Pt_2(4-mpyt)$_4$] give very similar Pt—Pt distances. The structure of *trans*-[Pt_2(4-mpyt)$_4I_2$] is shown in Fig. 14.

E. PLATINUM DIMERS WITH PYROPHOSPHITES AS BRIDGING LIGANDS

The pyrophosphite (pop) complexes are the most thoroughly studied among lantern-type diplatinum complexes (*6–8*). The preparative

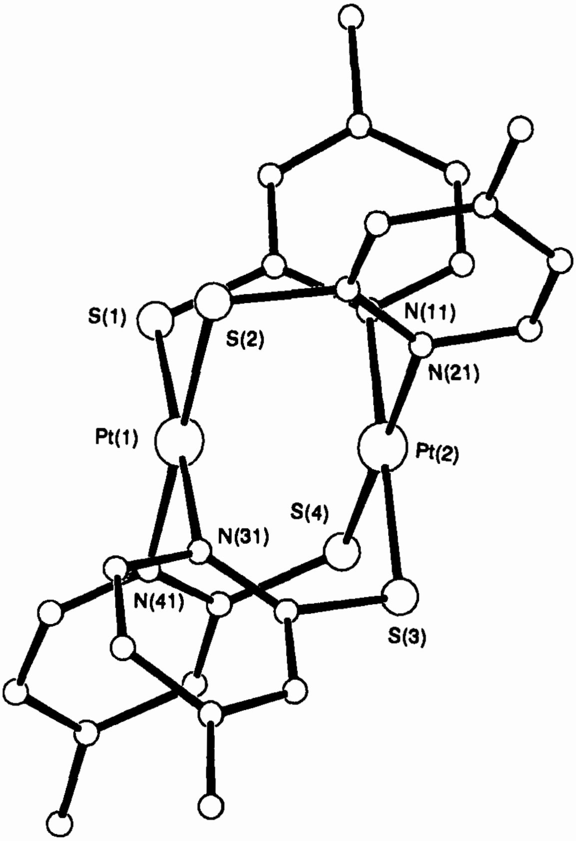


FIG. 12. ORTEP diagram of *cis*-[Pt_2(4-mpyt)$_4$].

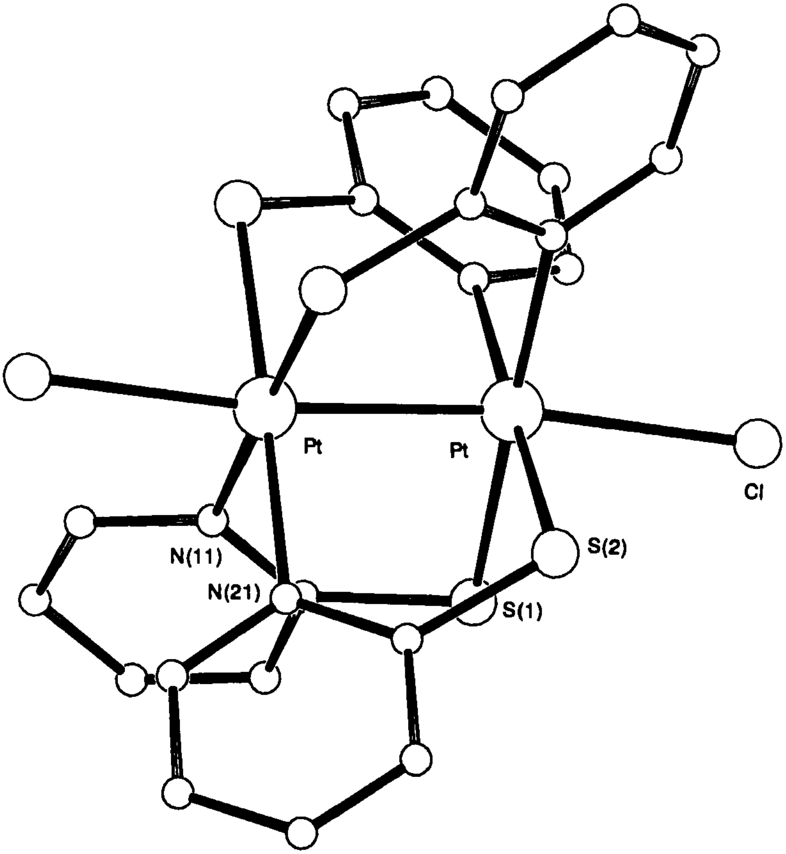


FIG. 13. ORTEP diagram of *cis*-$[Pt_2(pyt)_4Cl_2]$.

methods used for the luminescent Pt(II) complex include the reaction of $K_2[PtCl_4]$ with H_3PO_3 in aqueous solution (*5, 49, 50*).

$$[PtCl_4]^{2-} + H_3PO_3 \xrightarrow[H_2O\,(110^\circ C)]{} [Pt_2(H_2P_2O_5)_4]^{4-}$$

Oxidative addition reactions of halogens (X_2) with the Pt(II) complex in aqueous solution give the corresponding Pt(III) dimers with X^- at both axial positions (*51, 52*).

$$[Pt_2(H_2P_2O_5)_4]^{4-} \xrightarrow[H_2O]{X_2} [Pt_2(H_2P_2O_5)_4X_2]^{4-}$$

The mixed-valence Pt(II,III) dimers, $K_4[Pt_2(H_2P_2O_5)_4X]$, have also been isolated from the 1:1 mixture of the Pt(II) and Pt(III) dimers or a partial oxidation product of the Pt(II) dimer (*52, 53*). These mixed-valence complexes are unstable in solution to disproportionation to give the Pt(II) and Pt(III) dimers.

X-ray crystal structures of Pt(II) and several Pt(III) complexes with various axial ligands have been determined (see Table I). The Pt—Pt distance of the Pt(II) dimer is the longest among lantern-type platinum dimers (2.925(1) and 2.949(0) Å for pop ligand and 2.9801(2) Å for the related pcp ligand) (*5, 52, 54, 55*). On the contrary, those of the Pt(III) dimers span the range 2.676–2.782 Å. The mixed-valence Pt(II,III) di-

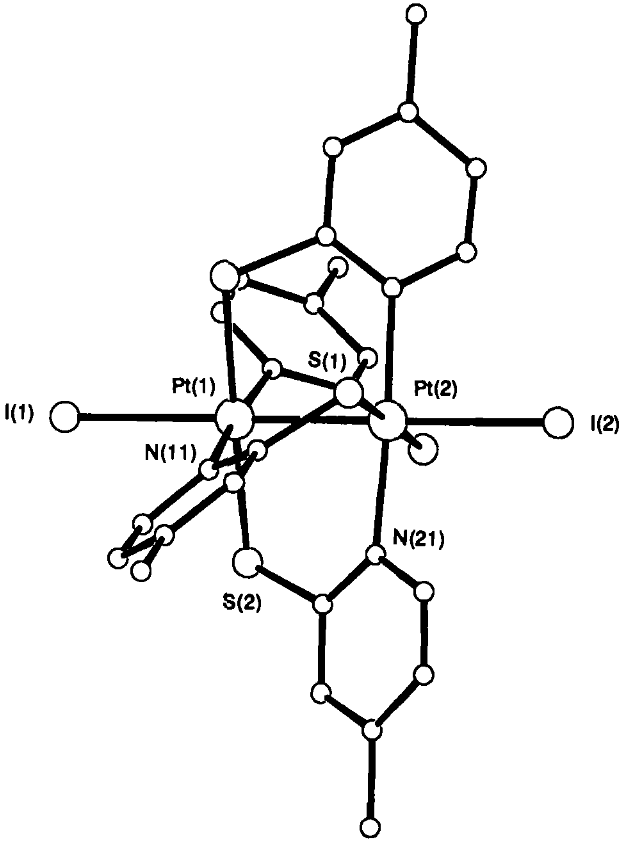


FIG. 14. ORTEP diagram of *trans*-$[Pt_2(4\text{-mpyt})_4I_2]$.

mers possess infinite chain structures, with each dimer unit connected by X^- (*52, 56–58*). The Pt—Pt distances are between those for the Pt(II) and Pt(III) dimers. The twist angles are small and independent of the oxidation state, as implied by the small differences between the ligand bite and the Pt—Pt distances.

F. PLATINUM DIMERS WITH OTHER BRIDGING LIGANDS

Although various dinuclear and oligonuclear Pt complexes of N,O-bridging ligands such as 2-hydroxypyridine (α-pyridone) (*59–62*), α-pyrrolidone (*63, 64*), pyrimidines (*65*), and other amides (*66–68*) have been reported, they are mostly of the doubly bridged type. The lantern-type structure has been postulated for the acetamide complex (*69, 70*). Except for this, no quadruply bridged complex has been identified so far with these bridging ligands. This is probably because the quadruply bridged structure would be highly stressed by the short bite distance of these ligands, as was observed for the tetrakis(acetato) complex. The novel cyclic, tetranuclear Pt(II) complex, $[\{Pt(en)(uracilato)\}_4](NO_3)_4$, was also reported (*71*).

G. PALLADIUM DIMERS

Compared with the extensive chemistry of the quadruply bridged platinum dimers, information on the palladium dimers is limited. One reason for this situation is that the tervalent oxidation state of palladium is very unstable. According to the general trend of redox properties of the second and third transition elements, palladium in the second transition series has more difficulty accessing the higher oxidation state than the third transition counterpart. The first successful preparation of the quadruply bridged palladium(III) dimer has appeared (*72*). Furthermore, the preferences of the types of ligands forming the quadruply bridged dimetal complexes are different between the two elements. No dipalladium complex is known with O,O′-bridging ligands such as sulfate and phosphate, which are particularly well established in the chemistry of the diplatinum(III) complexes (see section II—A). However, the N,O-bridging ligands, which do not give a quadruply bridged diplatinum complex, afford some stable dipalladium(II) complexes. It seems that palladium prefers nitrogen donor to oxygen-donor ligands.

Ligands that provide the dipalladium complexes are dithiocarboxylates (RCS_2^-), 1,3-benzothiazole-2-thiol (bttzH), 1,3-diphenyltriazen (dptH), *N,N*′-di-*p*-tolylformamidinate (form), *N,N*′-diphenylbenzamidine (dpbH), 6-substituted 2-hydroxypyridines (6-methyl-2-hydroxypyridine (mhpH) and 6-chloro-2-hydroxypyridine (chpH)), and pyridine-2-thiol (pytH) and its derivatives.

Reaction of dithioacetic acid with $K_2[PdCl_4]$ in ether followed by recrystallization from benzene gave crystals (*form A*) composed of $[Pd(CH_3CS_2)_2]$ and $[Pd_2(CH_3CS_2)_4]$ (*73, 74*). Recrystallization of *form* A from CS_2 at room temperature provides a pure sample of the dimer (*form B*). It was found that the sublimation of *form* A or *form* B at 190°C and 10^{-3} Torr gives partially polymerized complexes (*form C*). By contrast, $PhCS_2^-$ formed a quadruply bridged dipalladium(II) complex selectively (*75*). The Pd ··· Pd distance (2.738(1) Å) in $[Pd_2(CH_3CS_2)_4]$ is slightly shorter than the corresponding distance of the platinum dimer (2.767(1) Å) (Table I). Similar trends are seen for other isostructural complexes of the platinum(II) and palladium(II) dimers with $PhCS_2^-$ and pyt as ligands. Vibrational spectra of dithioacetao complexes have been reported (*36*).

When an aqueous solution of $K_2[PdCl_4]$ is mixed with Hbttz in a water–ethanol mixture, the palladium(II) dimer $[Pd_2(bttz)_4]$ is obtained (*76*).

$$[PdCl_4]^{2-} + \mathrm{Hbttz} \longrightarrow [Pd_2(bttz)_4]$$

However, when $K_2[PdCl_4]$ and 3 *M* sodium acetate in chilled water were mixed with Hdpt in methanol, the mononuclear complex $[Pd(dpt)_2(Hdpt)_2]$ is precipitated. This initial product can be converted to $[Pd_2(dpt)_4]$ on refluxing in acetone (*77*).

$$[PdCl_4]^{2-} + \mathrm{Hdpt} \xrightarrow[CH_3CO_2Na/H_2O]{} [Pd(dpt)_2(Hdpt)_2]$$

$$[Pd(dpt)_2(Hdpt)_2] \xrightarrow[\Delta]{} [Pd_2(dpt)_4]$$

These two dimeric Pd(II) complexes, $[Pd_2(bttz)_4]$ and $[Pd_2(dpt)_4]$, have been structurally analyzed and give Pd ··· Pd distances of 2.745(1) and 2.5626(7) Å, respectively (*9, 76*).

The reaction of palladium(II) acetate with Li(form) in THF gives $[Pd_2(form)_4]$, which undergoes one-electron oxidation upon addition of $AgPF_6$ in dichloromethane to $[Pd_2(form)_4]PF_6$ (*78, 79*).

$$Pd(CH_3CO_2)_2 + 2Li(form) \xrightarrow[\text{ca. 25°C}]{THF} (1/2)[Pd_2(form)_4] + 2CH_3CO_2Li$$

$$[Pd_2(form)_4] + AgPF_6 \xrightarrow[CH_2Cl_2]{} [Pd_2(form)_4]PF_6 + Ag$$

The Pd ··· Pd distance (2.637(6) Å) of the oxidized species is longer than that in $[Pd_2(form)_4]$ (2.622(3) Å) and is not consistent with the Pd—Pd direct bonding interaction in the former. An EPR study has indicated that ligand-localized oxidation rather than oxidation at the metal center is occurring. This view is supported by the molecular orbital calculations for a simplified model of this complex (*79*).

The *N,N′*-diphenylbenzamidinate (dpb) complex $[Pd_2(dpb)_4]$ is also known (*80*). This was prepared similarly to the *form* complex. The initial product is a doubly bridged dimer, $[Pd(dpb)]_2(\mu\text{-dpb})_2$, which after refluxing in methanol gives the quadruply bridged dimer $[Pd_2(dpb)_4]$.

$$Pd(CH_3CO_2)_2 + Li(dpb) \xrightarrow[\text{r.t.}]{CH_2Cl_2} \xrightarrow[\text{r.t.}]{\text{MeOH}} [(dpb)Pd]_2(\mu\text{-dpb})_2$$

$$[(dpb)Pd]_2(\mu\text{-dpb})_2 \xrightarrow[\Delta]{\text{MeOH}} [Pd_2(dpb)_4]$$

Dipalladium(II) complexes with N,O-bridging ligands, mhp and chp, were prepared by reaction of palladium(II) acetate with Na(mhp) or Na(chp) in dichloromethane (*81, 82*). Recrystallization of the former from methanol gives the *trans*-isomer exclusively. However, recrystallization from chloroform gives a sample containing the *cis*-isomer.

$$\begin{tikzcd}
Pd(CH_3CO_2)_2 + 2Na(mhp) \arrow[r, "CH_2Cl_2"'] & \text{orange–brown solid} \arrow[r, "\text{MeOH}"'] \arrow[dr, "CHCl_3"'] & trans\text{-}[Pd_2(mhp)_4] \\
 & & cis\text{- + }trans\text{-}[Pd_2(mhp)_4]
\end{tikzcd}$$

It is interesting that the ligands form, chp, and mhp, with much shorter bite distances, give stable quadruply bridged dipalladium(II) complexes having relatively long Pd—Pd distances. Corresponding diplatinum(II) complexes that would require slightly longer metal–metal distance are not known with these ligands.

The reaction of palladium(II) acetate with pytH in dioxane at room temperature gives selectively the *cis*-isomer of the Pd(II) dimer $[Pd_2(pyt)_4]$ (*83, 84*). By contrast, refluxing of the mixture of $[PdCl_2(CH_3CN)_2]$ and pytH in dioxane gives the mononuclear Pd(II) complex $[Pd(pytH)_4]Cl_2$. This monomer is a very useful starting material for the preparation of mixed-metal complexes with the pyt ligand (see section II—I). The monomer can be converted into $[Pd_2(pyt)_4]$ by treating it with aqueous potassium hydroxide solution. An attempt to oxidize $[Pd_2(pyt)_4]$ to the Pd(III) dimer with I_2 was unsuccessful. The tetranuclear palladium(II) complex $[Pd_4I_2(pyt)_6]$ was obtained instead.

$$\mathrm{Pd(CH_3CO_2)_2 + 2pytH \xrightarrow[\text{dioxane}]{} [Pd_2(pyt)_4]}$$

$$\mathrm{[PdCl_2(CH_3CN)_2] + 4pytH \xrightarrow[\text{dioxane}/\Delta]{} [Pd(pytH)_4]Cl_2 \xrightarrow[\text{1N-KOH aq.}]{} [Pd_2(pyt)_4]}$$

$$\mathrm{2[Pd_2(pyt)_4] + I_2 \longrightarrow [Pd_4I_2(pyt)_6] + bis(2\text{-}pyridyl)disulfide}$$

Exclusive formation of the geometrical *cis*-isomer for the pyt complex is in contrast with the preference of the *trans*-isomeric structure of the mhp and chp complexes. Steric hindrance at the 6-position of pyridine derivatives is considered to be responsible for the different geometrical isomerism.

Bear and co-workers reported that $[Pd_2(dpb)_4]$ could be oxidized to the Pd(III) state by removing electrons from the metal-based molecular orbital (*80*). However, the Pd(III) dimer with direct Pd—Pd bonding interaction has never been reported. Ooi and co-workers eventually prepared the first isolated example of a quadruply bridged dipalladium(III) complex, $[Pd_2(pyt)_4Cl_2]$, by reaction of $[Pd_2(pyt)_4]$ with $C_6H_5I{\cdot}Cl_2$ in chloroform at 0°C (*72*). The reaction temperature is critical for the successful isolation of the Pd(III) dimer; it slowly decomposes at room temperature.

$$\mathrm{[Pd_2(pyt)_4] + C_6H_5I{\cdot}Cl_2 \xrightarrow[CHCl_3]{} [Pd_2(pyt)_4Cl_2]}$$

X-ray analysis of $[Pd_2(pyt)_4Cl_2]$ disclosed that it is isostructural with $[Pt_2(pyt)_4Cl_2]$ (Fig. 15). The Pd—Pd distance (2.528(2) Å) is very close to the corresponding distance of the platinum dimer (2.532(1) Å), and the existence of a Pd—Pd single bond is indicated.

H. Nickel Dimers

A member of the first transition series of the group 10 elements, nickel, seems to have less of a tendency to form dinuclear or oligonuclear complexes compared with palladium and platinum. This is probably the consequence of the higher stability of the octahedral terms of nickel(II). The known quadruply bridged dinickel complexes are those of carboxylates, dithiocarboxylates, 1,3-diphenyltriazen (Hdpt), thiobenzoate, and *N,N'*-di-*p*-tolylformamidinate (form).

A nickel(II) dimer, $[Ni_2(CH_3CS_2)_4]$, precipitates immediately from a mixture of nickel chloride and dithioacetic acid (*85, 86*). The nickel(II) dimer is oxidized to the mixed-valence state, $[Ni_2(CH_3CS_2)_4I]$, upon reacting with a half equivalent amount of iodine in CS_2 solution (*86*). An attempt to obtain the Ni(III) dimer $[Ni_2(CH_3CS_2)_4I_2]$ was not successful.

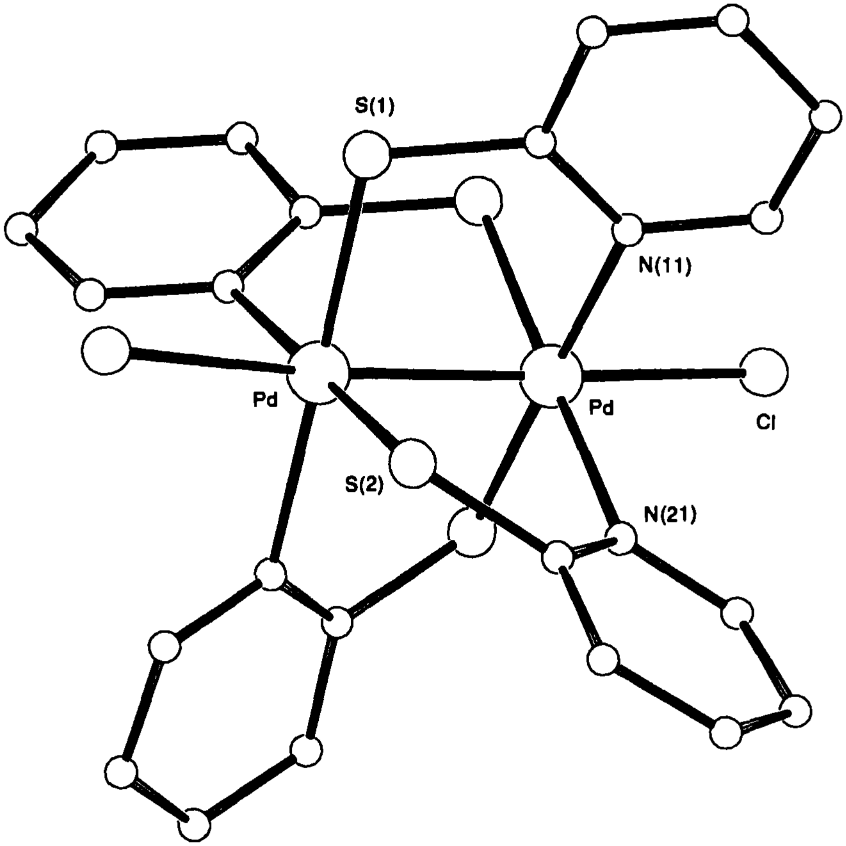


FIG. 15. ORTEP diagram of *cis*-[$Pd_2(pyt)_4Cl_2$].

$$NiCl_2 + CH_3CS_2H \longrightarrow [Ni_2(CH_3CS_2)_4]$$

$$[Ni_2(CH_3CS_2)_4] + (1/2)I_2 \xrightarrow[CS_2]{} [Ni_2(CH_3CS_2)_4I]$$

X-ray crystal structures of both dimers have been determined. The Ni—Ni distance of the mixed-valence dimer (2.514(5) Å) is shorter than that of the Ni(II) dimer (2.564(1) Å), suggesting stronger direct interaction between the two nickel ions. The crystal structure of [$Ni_2(CH_3CS_2)_4I$] consists of infinite chains of ··· $Ni_2(CH_3CS_2)_4$ ··· I ··· $Ni_2(CH_3CS_2)_4$ ··· I ···, which is similar to that of the Pt analogue. All the Ni atoms are equivalent. Vibrational spectra have been discussed (*36*). The reaction of nickel salt with dithiophenylacetic acid instead of dithioacetic acid also gives the quadruply bridged dinickel complex $[Ni_2(PhCH_2CS_2)_4]$ (*87, 88*). This compound has an Ni—Ni distance of 2.551(3) Å (75, 89).

The $[Ni_2(dpt)_4]$ complex was prepared by refluxing $[Ni(dpt)_2(py)_2]$ (*90*) in toluene for 3 hr or its thermal decomposition in the solid state at 120–130°C for 10–15 hr (*77*). The very short Ni—Ni distance (2.395(3) Å) is noted (*9, 10*).

$$[Ni(dpt)_2(py)_2] \xrightarrow[\Delta]{} [Ni_2(dpt)_4]$$

The reaction of nickel chloride and thiobenzoic acid in ethanol in the presence of sodium hydroxide gave $[Ni_2(PhCOS)_4]$ (*91*).

$$NiCl_2{\cdot}6H_2O + PhCOSH \xrightarrow[NaOH/EtOH]{} [Ni_2(PhCOS)_4]$$

X-ray structural analysis has revealed that the geometries of two nickel atoms are different; one axial position is occupied by coordinated ethanol, whereas the other position is vacant (*92, 93*). The Ni ··· Ni distance in the dimer is 2.503(4) Å.

The form complex $[Ni_2(form)_4]$ was obtained by refluxing a solution of nickel bromide and Li(form) in THF for 24 hr (*78, 79*). The dimer undergoes one-electron oxidation by $[Ag(CH_3CN)_2]BF_4$ in dichloromethane.

$$NiBr_2 + 2Li(form) \xrightarrow[THF/\Delta]{} (1/2)[Ni_2(form)_4] + 2LiBr$$

$$[Ni_2(form)_4] + [Ag(CH_3CN)_2]BF_4 \xrightarrow[CH_2Cl_2]{} [Ni_2(form)_4]BF_4 + Ag + 2CH_3CN$$

Structures of both $[Ni_2(form)_4]$ and $[Ni_2(form)_4]BF_4$ have been determined. The crystal structure of $[Ni_2(form)_4]{\cdot}2H_2O$ is isostructural with that of $[Pd_2(form)_4]{\cdot}2H_2O$. Again the mixed-valence dimer has a shorter Ni—Ni distance (2.418(4) Å) than that of the Ni(II) dimer (2.485(2) Å). Interestingly, the torsion angle of the mixed-valence dimer (27.4°) is greater than that of Ni(II) dimer (16.8°), in spite of the smaller difference between the bite distance and the metal—metal distance. EPR measurement indicated that the metal centers are oxidized in this case.

The dinickel(II) complexes so far mentioned, $Ni_2(dpt)_4$ in particular, have rather short Ni ··· Ni distances; and some direct Ni—Ni bonding interaction has been suggested based on the mixing of *d* orbitals with upper *s* and *p* orbitals (*79*). The paramagnetic carboxylate bridged dimers are significantly different in that they have much longer Ni ··· Ni distances and contain pentacoordinated nickel ions with various axial ligands (*94–97*).

I. HETERODINUCLEAR COMPLEXES

Similar structural characteristics of the quadruply bridged dinuclear complexes of Pt(II), Pd(II), and Ni(II) indicate that the mixed-metal dinuclear complexes of these metal ions should be stable. However, probably because of the synthetic difficulties, only a few mixed-metal complexes of group 10 elements with such a structure have been prepared so far, although there are a number of examples having a doubly bridged structure (*98, 99*). For other metals, quadruply bridged mixed-metal complexes are known with the group 6 metal ions Cr, Mo, and W (*1, 100, 101*).

Ooi and co-workers adopted an elegant synthetic approach to the mixed-metal complexes of 4-methylpyridine-2-thiolate (4-mpyt). This approach includes the initial preparation of mononuclear complexes $[M(4\text{-mpytH})_4]Cl_2$ (M = Pt, Pd), in which all four 4-mpytH ligands coordinate to M^{II} with sulfur-donor atoms (*84, 102*). The structure of the mononuclear Pd(II) complex with nonsubstituted pyridine-2-thiolate, $[Pd(pytH)_4]Cl_2$, is shown in Fig. 16 (*84*). These mononuclear complexes can be further reacted with the second metal ion to give mixed-metal dinuclear complexes.

The first mixed-metal complex with a quadruply bridged structure, $[PtNi(4\text{-mpyt})_4(MeCN)]$, was prepared by the reaction of $[Pt(4\text{-mpytH})_4]Cl_2$ with nickel acetate in the presence of potassium bicarbonate in naphthalene as a solvent at 120°C (*102*).

$$[PtCl_4]^{2-} + 4(4\text{-mpytH}) \xrightarrow[\text{toluene}/\Delta]{} [Pt(4\text{-mpytH})_4]Cl_2$$

$$[Pt(4\text{-mpytH})_4]Cl_2 + Ni(CH_3COO)_2$$

$$\xrightarrow[\text{naphthalene}/120^\circ C]{KHCO_3} \xrightarrow[MeCN/CH_2Cl_2]{\text{silica gel}} [PtNi(4\text{-mpyt})_4(MeCN)]$$

Structural analysis disclosed that the PtNi complex takes a 4S geometry with the Pt atom coordinated by four sulfur atoms (Fig. 17). Acetonitrile is coordinated to the Ni site at the axial position to make the nickel ion hexacoordinated, including the neighboring platinum ion. The mean Pt ··· Ni distance (2.539 Å; Table I) is considerably shorter than the Pt ··· Pt distance of $[Pt_2(4\text{-mpyt})_4]$.

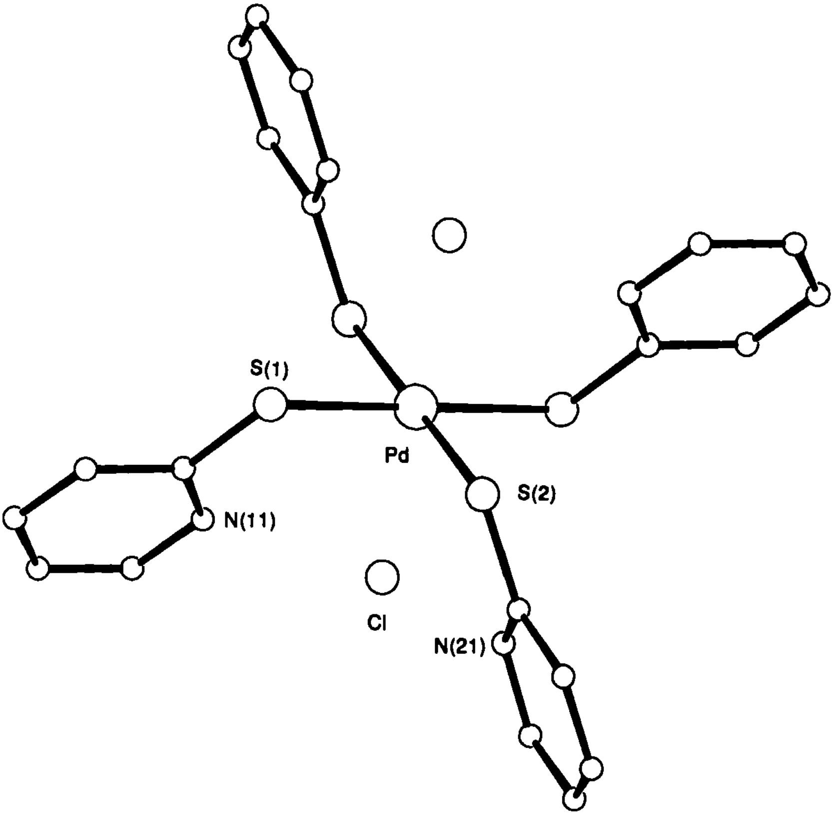


FIG. 16. ORTEP diagram of $[Pd(pytH)_4]Cl_2$.

The analogous PdNi complex, $[PdNi(4\text{-mpyt})_4(MeCN)]$, was prepared similarly (*103*). Again the Pd ··· Ni distance is short (2.541 Å). The nickel(II) dimer of pyridine-2-thiolate and its derivatives are not known, but the Ni ··· Ni distance of such complexes would be expected to be around 2.5 Å as judged from the data for the existing Ni(II) dimers (Table I). Therefore the Pt—Ni or Pd—Ni distance can be shorter than the average of the two corresponding homonuclear complexes. There may be some positive interaction between the two metal ions as discussed for $Pt_2(RCS_2)_4$ (*37*) and some Ni(II) dimers (*79*).

Corresponding PdPt complexes have been prepared as follows. A suspension of $PdCl_2$ and 4-mpytH in 2-methoxyethanol was heated at 80°C for 12 hr to give $[Pd(4\text{-mpytH})_4]Cl_2$, in which all 4-mpytH ligands coordinate to the Pd ion through the sulfur atom. The reaction of [Pd(4-

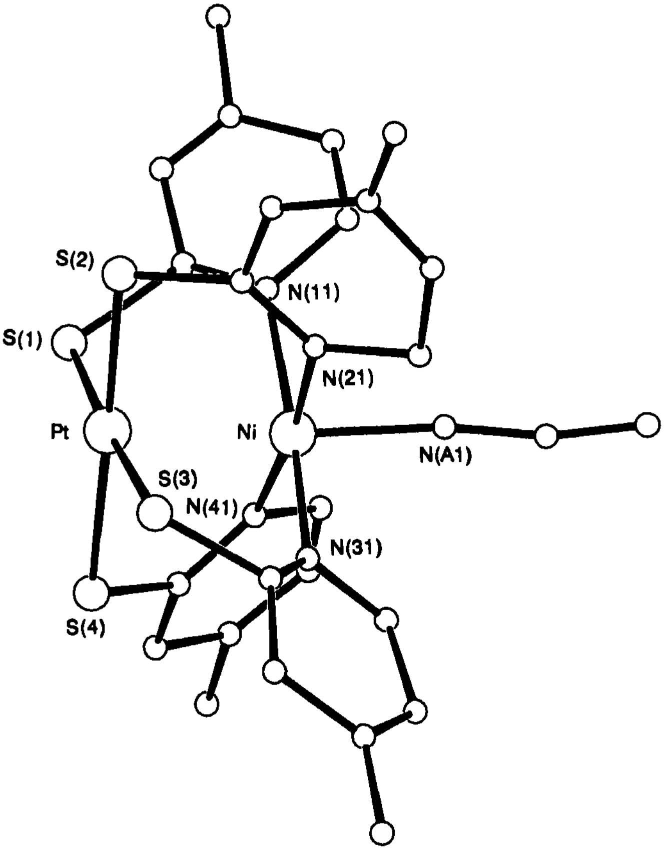


FIG. 17. ORTEP diagram of 4*S*-[PtNi(4-mpyt)$_4$(MeCN)].

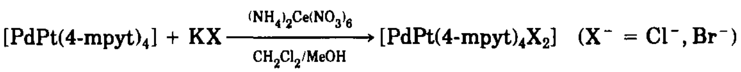
mpyt)$_4$]Cl$_2$ with [PtCl$_2$(py)$_2$] in methanol at 40°C for an hour followed by the addition of KHCO$_3$ in methanol gives fine orange crystals (*104*).

$$PdCl_2 + \text{4-mpytH} \xrightarrow[\text{2-methoxyethanol}]{} [Pd(\text{4-mpytH})_4]Cl_2$$

$$[Pd(\text{4-mpytH})_4]Cl_2 + [PtCl_2(py)_2] \xrightarrow[\text{KHCO}_3\text{/MeOH}]{} [PdPt(\text{4-mpyt})_4] + [Pd_2(\text{4-mpyt})_4]$$

The crystals are made up of two complexes that are statistically disordered with the composition [PdPt(4-mpyt)$_4$]$_{0.67}$[Pd$_2$(4-mpyt)$_4$]$_{0.33}$. The average structure (Fig. 18) is very similar to those of [Pt$_2$(4-mpyt)$_4$] (*47*) and [Pd$_2$(pyt)$_4$] (*84*).

Oxidation of the mixture by Ce(IV) in dichloromethane in the presence of halide ions gives the pure mixed-metal(III) complex [PdPt(4-mpyt)$_4$X$_2$] (X$^-$ = Cl$^-$, Br$^-$) (*104*). The two different metal ions are statistically disordered in crystals of [PdPt(5-mpyt)$_4$Cl$_2$]. The Pt—Pd distance is 2.568(1) Å. The structure (Fig. 19) is similar to that of the analogous homonuclear Pt(III) dimer [Pt$_2$(pyt)$_4$Cl$_2$] (*47*). It is therefore suggested that a Pd—Pt single bond exists in the mixed-metal(III) complex.



$$[\mathrm{PdPt(4\text{-}mpyt)_4}] + \mathrm{KX} \xrightarrow[\mathrm{CH_2Cl_2/MeOH}]{\mathrm{(NH_4)_2Ce(NO_3)_6}} [\mathrm{PdPt(4\text{-}mpyt)_4X_2}] \quad (\mathrm{X^-} = \mathrm{Cl^-}, \mathrm{Br^-})$$

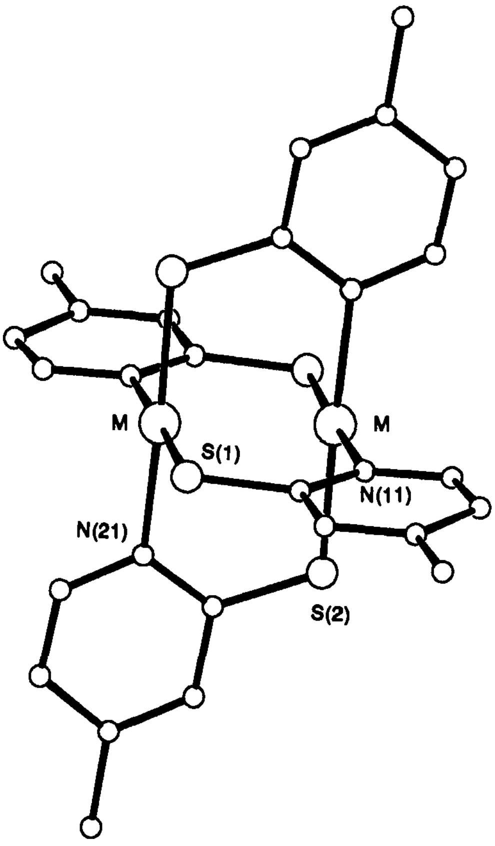


FIG. 18. ORTEP diagram of *cis*-[PdPt(4-mpyt)$_4$]$_{0.67}$[Pd$_2$(4-mpyt)$_4$]$_{0.33}$.

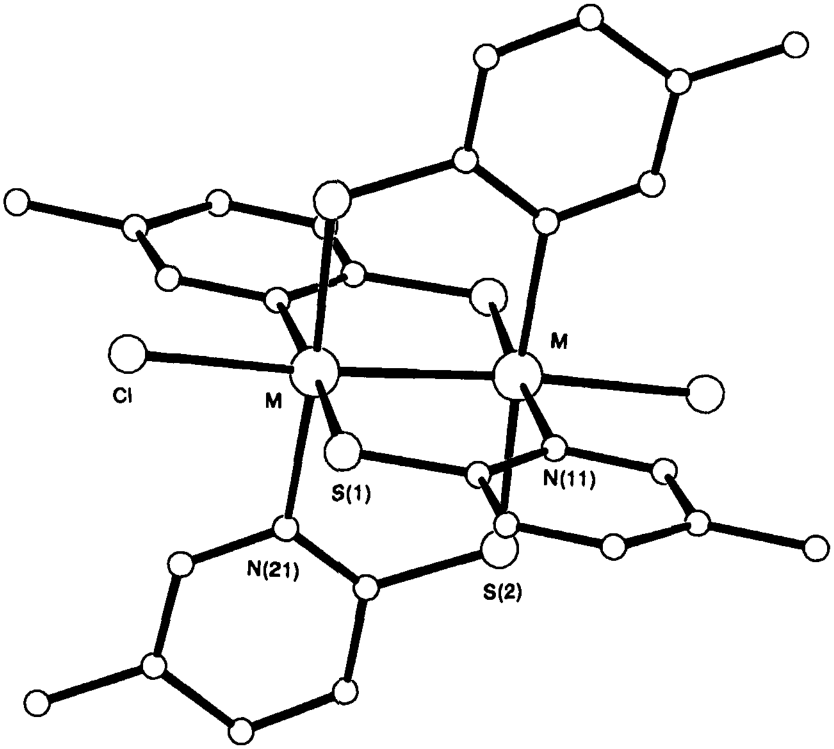


FIG. 19. ORTEP diagram of *cis*-[PdPt(5-mpyt)$_4$Cl$_2$].

J. STRUCTURAL CHARACTERISTICS OF THE QUADRUPLY BRIDGED PLATINUM DIMERS

In this section, we will summarize the structural characteristics of the diplatinum complexes mainly in terms of ligand bite distances and the Pt—Pt bond length. The metal–metal distance is important primarily in considering metal–metal interaction, as already seen in the case of the Pt(III) and Pd(III) dimers. Although there is no formal direct metal–metal bond for the quadruply bridged d^8–d^8 dimers, relatively short distances found in some Pt(II), Pd(II), and Ni(II) dimers have been taken as evidence for the existence of some direct metal–metal interactions. The metal–metal distance is affected primarily by the bite distance of the bridging ligand, and also the axial ligand, which perturbs the metal–metal distance according to the ligand σ-donor strength. An increase in the ligand σ-donor strength could cause a weakening of the metal–metal bond via σ^* orbital participation (*105, 106*). The rigidity of the bridging ligand also influences the metal–metal distance. Thus, the less rigid pyrophosphite (pop) ligands in $[Pt_2(pop)_4X_2]^{n-}$ adjust the P—O—P angle in order to fit the required Pt—Pt distance; decrease in the Pt—Pt distance causes shortening of the bite distance (the P ··· P distance) (*107*).

A diagram of the correlation between the Pt(III)—Pt(III) distance and the ligand bite distance (calculated from the atomic parameters in the literature) is given in Fig. 2. A similar diagram for the quadruply bridged dimolybdenum(II) complexes with quadruple Mo—Mo bonds is also included in Fig. 2 for comparison. It is obvious from Fig. 2 that, although the Pt—Pt distance increases linearly (as much as 0.39 Å) with an increase in the bite distance (Δ = 0.73 Å) (Table I), the Mo—Mo distance is rather constant (Δ = 0.10 Å) (Table II) (*108, 135–147*). It should be noted that the range of bite distances is similar between the two series of the complexes (Δ = 0.77 Å for the molybdenum series). It is also seen in Table I that deviations of the metal atom from the coordination plane in the platinum complexes are remarkably small (<0.14 Å). Deviations in the case of the molybdenum complexes are as much as +0.43 Å, as found for $[Mo_2(S_2COC_2H_5)_4]$, which has the longest

TABLE II

STRUCTURAL DATA FOR SELECTED QUADRUPLY BRIDGED COMPOUNDS CONTAINING Mo(II)—Mo(II) QUADRUPLE BONDS

Compound[a]	Ligand type	Bite distance[b] (Å)	Mo—Mo distance (Å)	Deviation[b,c] (Å)	Twist angle[b] (°)	Reference
$[Mo_2(S_2COC_2H_5)_4]\cdot 2THF$	S—S	2.99	2.125(1)	0.43	1.3	*108*
$[Mo_2(S_2CPh)_4]\cdot 2THF$	S—S	2.95	2.139(2)	0.40	0.8	*135*
$[Mo_2(S_2CMe)_4]\cdot 2THF$	S—S	2.94	2.141(1)	0.40	0.4	*135*
$[Mo_2(dmmp)_4]\cdot CH_2Cl_2$	N—S	2.68	2.083(2)	0.30	1.1	*136*
$K_4[Mo_2(SO_4)_4]\cdot 2H_2O$	O—O	2.43	2.111(1)	0.16	0.3	*137*
$[Mo_2(map)_4]\cdot 2THF$	N—N	2.30	2.070(1)	0.12	1.6	*138*
$[Mo_2(chp)_4]$	N—O	2.27	2.085(1)	0.09	3.1	*139*
$[Mo_2(form)_4]$	N—N	2.27	2.085(4)	0.09	3.3	*140*
$[Mo_2(mhp)_4]\cdot CH_2Cl_2$	N—O	2.27	2.065(1)	0.10	1.3	*141*
$[Mo_2[(2,6\text{-xylyl})NC(CH_3)O]_4]\cdot 2CH_2Cl_2$	N—O	2.27	2.083(2)	0.09	0.7	*142*
$[Mo_2[pyNC(O)CH_3]_4]$	N—N	2.25	2.037(3)	0.11	0	*143*
$[Mo_2(glygly)_4]Cl_4\cdot 6H_2O$	RCO_2	2.23	2.106(1)	0.06	1.8	*144*
$[Mo_2(O_2CC(CH_3)_3)_4]$	RCO_2	2.23	2.088(1)	0.07	0.4	*145*
$[Mo_2(O_2CCH_3)_4]$	RCO_2	2.23	2.0934(8)	0.07	0.1	*146*
$[Mo_2(O_2CPh)_4]$	RCO_2	2.23	2.096(1)	0.06	0.3	*145*
$[Mo_2(\text{L-leu})_4]Cl_2(pts)_2\cdot 2H_2O$	RCO_2	2.21	2.111(1)	0.05	0.6	*147*

[a] Ligand abbreviations are as follows: dmmp, anion of 4,5-dimethyl-2-mercaptopyrimidine; map, anion of 2-amino-6-methylpyridine; chp, anion of 6-chloro-2-hydroxypyridine; form, anion of di-*p*-tolylformamidine; mhp, anion of 6-methyl-2-hydroxypyridine; glygly, glycylglycinate; L-leu, L-leucinate; pts, *p*-toluenesulfonate; $pyNC(O)CH_3$, anion of *N*-(2-pyridyl)acetamide.

[b] The mean value.

[c] The deviation of each molybdenum atom from the coordination plane defined by four donor atoms.

ligand bite distance (2.99 Å) (*108*). The small deviation found in the Pt(III) complexes is not simply the consequence of a wide range of Pt—Pt bond lengths but also of a twist of the two Pt coordination planes along the Pt—Pt axis. The latter adjusts the difference in the Pt—Pt distance and bite distance to some extent. Thus, the twist angles in the Pt(III) complexes of dithioacetate with a long bite distance are large (ca. 25°) and those in acetate with a short bite distance are very small (<5°). On the contrary, the twist angles of the Mo(II) dimers with quadruple bonds are always very small (<3.3°). These facts may be summarized as follows. In the case of the Pt(III) dimers, the twist of the coordination plane along the Pt—Pt axis is less constrained because the Pt—Pt interaction is of σ-type single bond origin. On the contrary, the Mo(II) dimers tend to take an eclipsed configuration because of the existence of the δ bond, and the twist of the coordination plane is difficult. Furthermore, the strong Mo—Mo quadruple bond is less flexible in adjusting the Mo—Mo distance, and large deviations of the Mo from the coordination plane result.

Table III classifies the bridging ligands by their bite distances and correlates them with the known oxidation states of the diplatinum complexes. When ligands with bite distances longer than ca. 2.7 Å react with Pt(II) salts, Pt(II) complexes are obtained. On the contrary, in those cases with a shorter bite distance than 2.7 Å, Pt(III) instead of Pt(II) dimers are obtained. Chlorine abstraction of $[Pt_2^{II}(pyt)_4]$ from chloroform to produce $[Pt_2^{III}(pyt)_4Cl_2]$ is taken as an intermediate phenomenon, and the bite distance of ca. 2.7 Å is considered a limit for

TABLE III

DEPENDENCE OF THE Pt OXIDATION STATE ON THE BITE DISTANCE OF THE BRIDGING LIGAND[a]

Ligand	Bite distance	Oxidation state of Pt
RCS_2^-	3.11–2.99	+2.0, +2.5, +3.0
$P_2O_5H_2^{2-}$	2.98–2.86	+2.0, +2.5, +3.0
$C_5H_4NS^-$, $C_6H_6NS^-$	2.74–2.71	+2.0, +3.0
$C_4H_3N_2S^-$, $C_4H_3N_2OS^-$	2.71	+2.0,[b] +3.0
PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$	2.56–2.52	+3.0
SO_4^{2-}	2.47–2.45	+3.0
$CH_3CO_2^-$, $CH_2CO_2^{2-}$	2.62–2.23	+3.0

[a] All references are given in Table I.

[b] The precursor Pt(II) complex can be isolated under oxygen-free conditions.

the preference of Pt(II) or Pt(III) oxidation states (*109*). It is also interesting that unbridged diplatinum(III) compounds have a Pt—Pt bond of 2.694(1) Å in $[Pt_2Cl_6(NH{=}C(OH)C(CH_3)_3)_4]$ (*110*) and 2.6964(5) Å in $[Pt_2(C_8H_{13}N_2O_2)_4Cl_2]$ (*111*). The Pt(III) complexes with ligands having longer bite distance than 2.7 Å are prepared by oxidizing the corresponding Pt(II) dimers.

III. Spectroscopic Properties and Electronic Structure

The electronic structures of lantern-type Pt(III) dimers are discussed on the basis of a general scheme for dimers with a d^7–d^7 electronic configuration, as depicted in Fig. 20. HOMO is considered either the $d\pi^*$ or the $d\delta^*$ orbital of the Pt—Pt single bond. The LUMO is usually $d\sigma^*$ orbital. In the case of the Pt(II) dimers, HOMO is now $d\sigma^*$ orbital

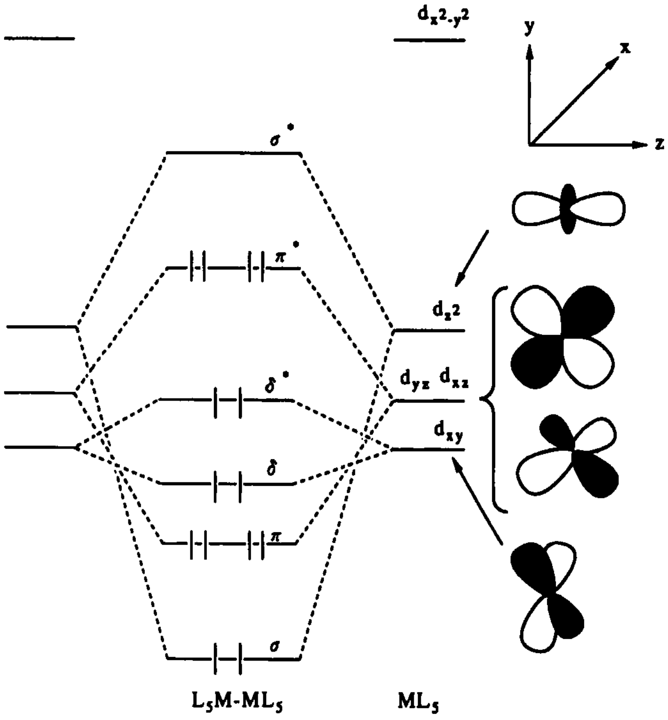


FIG. 20. MO diagram for the lantern-type dinuclear complex with the d^7–d^7 electronic configuration.

and no transitions associated with the Pt—Pt bond in this scheme is possible.

A. ELECTRONIC ABSORPTION SPECTRA

The electronic spectrum of the Pt(II) complex $[Pt_2(pop)_4]^{4-}$ shows two major absorption peaks at 367 nm (log ε = 4.54) and 435 nm (log ε = 2.04). These are assigned to singlet and triplet $d\sigma^* \rightarrow p\sigma$ transitions, respectively. The triplet excited state gives strong emission, and the photochemical and photophysical properties have been extensively investigated (*6–8*). The complexes $[Pt_2(RCS_2)_4]$ have intense visible absorption, which has been assigned to the transition associated with metal—metal interaction through $d\sigma$–$p\sigma$ mixing (*37*).

Spectral data for the quadruply bridged Pt(III) complexes are summarized in Table IV. Among the complexes in the table, those with pop, sulfate, and phosphate as bridging ligands have been extensively studied. Most of the bands in the table are believed to correspond to transitions to an empty $d\sigma^*$ orbital from lower filled energy orbitals. The most prominent feature of the electronic absorption spectra is the existence of a strong absorption peak in the ultraviolet region. The strong bands were initially assigned to the $d\sigma \rightarrow d\sigma^*$ transitions, but this was reconsidered later (*8, 112, 113*). Commonly observed for the complexes with three different bridging ligands are significant shifts in the peak position with the change in the type of axial ligands. Thus the complexes with axial aqua ligands exhibit the peak at 245, 225, and 225 nm, for the pop, sulfate, and phosphate bridging complexes, respectively. The bands shift to a lower energy region when the aqua ligands are replaced by anionic or other neutral donor ligands. For example, the chloro complexes show the bands at 282, 301, and 302 nm. Similarly, the bands of the bromo complexes are at 305, 348, and 339 nm. There is a trend that the band shifts to a lower energy region as the donor ability of the axial ligand increases (*8*). In the case of the phosphate complexes, the band even shifts to 446 nm with mercaptopropionate as an axial ligand (*18*).

It has been suggested for the pop complexes that the band is a ligand-to-metal charge transfer transition, σ(axial ligand) $\rightarrow d\sigma^*$, except for the complexes with diaqua or weakly donating axial ligands. The $d\sigma \rightarrow d\sigma^*$ transition has been suggested to appear at around 215 nm (*112*). Similar assignments have been made for the strong bands of the sulfate and phosphate bridged complexes (*112, 113*). It has also been pointed out for the phosphate complexes that if the significant difference in the Pt—Pt bond length between the pop and the phosphate complexes is considered, the $d\sigma \rightarrow d\sigma^*$ transition should be in an even higher energy region provided that the $d\sigma \rightarrow d\sigma^*$ assignment of the pop complex is correct (*112*).

The assignments of $(d\sigma,\sigma(X)) \rightarrow d\sigma^*$ transitions for the two series of complexes (sulfate and phosphate) with shorter Pt—Pt distances have been claimed to be inconsistent with the recent work of magnetic circular dichroism (MCD) spectral measurements (*114*). Tentative assignments are LMCT transitions from the bridging and axial ligands for the diaqua and dihalo complexes, respectively, to possibly a $\sigma^*(PtO_4)$ orbital. Results of the earlier MCD studies on the strong bands of the pop complexes appear to be consistent with the above assignments (*115*). The different assignments from the pop complexes are considered to be due to the different Pt—Pt bond distances. Again the $d\sigma \rightarrow d\sigma^*$ transitions appear in a much higher energy region (*115*). Electronic spectra of other Pt(III) dimers have not been discussed extensively except for tentative assignments of $d\sigma \rightarrow d\sigma^*$ transition to the strongest bands.

B. VIBRATIONAL SPECTRA

Core vibrational frequencies obtained by Raman or resonance Raman spectrophotometric technique are summarized in Table V (*53, 113, 116–118*). The ν(Pt—Pt) bands for the pop complexes $[Pt_2(pop)_4]^{4-}$ $(Pt(II)_2)$, $[Pt_2(pop)_4X]^{4-}$ $(Pt(II,III)_2)$, and $[Pt_2(pop)_4X_2]^{4-}$ $(Pt(III)_2)$ increase in the order expected from increasing Pt—Pt interaction (*53*). Resonance Raman spectra have been used frequently for the assignment of the electronic transitions of complexes as listed in the table. Also, observation of the vibrational structure in the low-temperature luminescence spectra coupled with the data in the table has been useful for considering the nature of the transition of these diplatinum complexes. The resonance Raman spectra at the intervalence band of the three mixed-valence complexes, which are stable only in the solid state, indicate that $[Pt_2(pop)_4Cl]^{4-}$ is a localized valence species and the bromo and iodo analogues are nearly delocalized valence species (*53*).

C. PHOTOCHEMICAL AND PHOTOPHYSICAL PROPERTIES

The pyrophosphite bridged lantern-type platinum(II) complexes are known to give strong emissions. Analogous complexes with methylenebis(phosphonite) as a bridging ligand are also emitters. Their electronic structures and associated reactivities have been extensively studied and are summarized in a review article (*8*). Some further information

TABLE IV

ELECTRONIC ABSORPTION SPECTRAL DATA OF SOME DIMERIC Pt(III) COMPLEXES, $[Pt_2(BL)_4X_2]^{n-}$

BL	X	Solvent	λ_{max}/nm (ε/cm^{-1} mol^{-1} dm^3)	Reference
SO_4^{2-}	H_2O	0.1 *M* H_2SO_4	226(27400), 347(650), 381(790), 466(89)sh	*114*
	H_2O	1 *M* H_2SO_4	224(28700), 260(1200)sh, 348(770), 380(900), 465(150)sh	*113*
	Cl^-	2.0 *M* HCl–0.05 *M* H_2SO_4	301(34300), 404(1980), 478(200)	*114*
	Cl^-	0.5 *M* LiCl–1 *M* H_2SO_4	220(20000)sh, 298(33500), 401(1850), 480(300)sh	*113*
	Br^-	2.0 *M* NH_4Br–1.0 *M* H_2SO_4	308(14800), 348(40400), 426(2350)	*114*
	Br^-	0.5 *M* LiBr–1 *M* H_2SO_4	345(31100), 420(2200)sh, 500(400)sh	*113*
	NH_3	0.225 *M* $(NH_4)_2SO_4$–0.590 *M* NH_3	261(23000), 318(2600)	*114*
	OH^-	0.00875 *M* NaOH	276(25000), 347(2400), 426(490)	*114*
	$(CH_3)_2S$	0.0156 *M* $(CH_3)_2S$	338(41000), 376(20100)	*114*
HPO_4^{2-}	H_2O	0.10 *M* $HClO_4$	225(24300), 330(474), 393(740), 498(65)	*114*
	Cl^-	2.0 *M* HCl–0.05 *M* $HClO_4$	302(40000), 409(2000), 500(155)	*114*
	Br^-	1.9 *M* NH_4Br–0.05 *M* $HClO_4$	299(12900), 339(41000), 410(2000), 517(205)	*114*
	OH^-	Water	266	*18*
	S-Me–L-cys	Water	340(23770)	*18*

	Methione	Water	344(24200)	*18*
	Thiodiethanol	Water	348(24650)	*18*
	Thiodipropionate	Water	344(24820)	*18*
$(CH_3COO)_2(CH_2COO)_2$	Cl^-	Water	220sh, 270sh, 372(780), 436(90)	*24*
$(CH_3COO)_3(CH_2COO)$	Cl^-	0.2 *M* KCl	280(20400), 405(1350), 474(170)sh	*25*
	Br^-	0.2 *M* KBr	328(21300), 400(2000)sh, 490(240)sh	*25*
	H_2O	0.1 *M* $HClO_4$	225(15600)sh, 380(730), 460(120)sh	*25*
$H_2P_2O_5{}^{2-}$	H_2O	0.1 *M* H_2SO_4	245(25000), 320	*50*
	Cl^-	Water	282(48400), 345(8190), 390	*50*
	Br^-	Water	305(55400), 345(11780)	*50*
	$NO_2{}^-$	Water	312(22000), 360(12100)sh, 470(650)	*50*
	I^-	CH_3CN	338(42930), 435(15930)	*50*
	SCN^-	Water	337(43600), 367sh, 480(740)	*50*
pyt($C_5H_4NS^-$) (*cis*-isomer)	Cl^-	$CHCl_3$	267(71600), 298(38700)sh, 375(3980), 426(2400)sh, 473(1500)sh	*47*
	Br^-	$CHCl_3$	269(59300), 314(32900), 345(17000)sh, 392(4700)sh, 452(2830), 498(2930)	*47*
	I^-	$CHCl_3$	274(58800), 317(31500), 384(19800), 444(8900), 556(10000)	*47*
	SCN^-	$CHCl_3$	272(52700), 312(26900), 380(18400), 458(5320), 498(5640)	*47*

TABLE V

RAMAN AND RESONANCE RAMAN BANDS (cm^{-1}) FOR THE LANTERN-TYPE DIPLATINUM COMPLEXES

	ν(Pt—Pt)	ν(Pt—BL)[a]	ν(Pt—X)[b]	Reference
$[Pt_2(SO_4)_4(H_2O)_2]^{2-}$		345, 318		*113*
$[Pt_2(SO_4)_4Cl_2]^{4-}$	214	350, 320	296	*113*
$[Pt_2(SO_4)_4Br_2]^{4-}$	157	330, 293	228	*113*
$[Pt_2(SO_4)_4(H_2O)_2]^{2-}$	297			*116*
$[Pt_2(SO_4)_4Cl_2]^{4-}$	211		340	*116*
$[Pt_2(SO_4)_4Br_2]^{4-}$	210, 193			*116*
$[Pt_2(SO_4)_4(CN)_2]^{4-}$	215			*116*
$[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$	291			*116*
$[Pt_2(HPO_4)_4(CN)_2]^{4-}$	211			*116*
$[Pt_2(HPO_4)_4(NH_3)_2]^{2-}$	226		421	*116*
$[Pt_2(P_2O_5H_2)_4]^{4-}$	115			*53*
$[Pt_2(P_2O_5H_2)_4Cl]^{4-}$	119, 155		301	*118*
$[Pt_2(P_2O_5H_2)_4Br]^{4-}$	116.5, 122		211	*118*
$[Pt_2(P_2O_5H_2)_4Cl]^{4-}$	152.3	339	291.3	*53*
$[Pt_2(P_2O_5H_2)_4Br]^{4-}$	117, 122		210	*53*
$[Pt_2(P_2O_5H_2)_4I]^{4-}$	100		185	*53*
$[Pt_2(P_2O_5H_2)_4Cl_2]^{4-}$	158		305	*53*
$[Pt_2(P_2O_5H_2)_4Br_2]^{4-}$	133		223	*53*
$[Pt_2(P_2O_5H_2)_4I_2]^{4-}$	105.4	340	189.1	*53*

[a] BL represents the bridging ligand.
[b] X represents the axial ligand.

is available in addition to the reviews (*119–124*). We will not discuss the electronic structure of the pop complexes except for stating that the relevant electronic transition is between the $d\sigma^*$ (HOMO) and the $p\sigma$ (LUMO) orbitals. Other Pt(II) complexes that contain ligands with sulfur donor atom(s) have not been reported to give emissions. This is probably because of the existence of lower energy transitions of the intraligand or charge-transfer type for the complexes with sulfur-containing ligands.

Among the lantern-type Pt(III) complexes, the pop, sulfate, and phosphate complexes are known to give emissions on irradiation with ultraviolet light. Strong red emission was observed at 77 K for $[Pt_2(pop)_4X_2]^{4-}$ ($X^- = Cl^-$, Br^-, and SCN^-) and $[Pt_2(pop)_4(py)_2]^{2-}$ in $CH_3OH—C_2H_5OH$ glasses (*125*). A progression with an average vibrational spacing of 125 cm^{-1} was observed with the bromo complex, and it was concluded that emissive excited state is highly distorted along the Pt—Pt axis. Photocatalyzed axial ligand substitution (*126*) and reductive elimination of the axial ligand as X_2 (= CH_3I, $(SCN)_2$, I_2, Cl_2, Br_2, and (imidazole)$_2$) to give $[Pt_2(pop)_4]^{4-}$ were reported (*127*).

Photophysical properties are more thoroughly investigated with the phosphate-bridged complexes (*112*). Three phosphate-bridged complexes, $[Pt_2(HPO_4)_4X_2]^{4-}$ (X^- = Cl^-, Br^-) and $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$, are reported to exhibit red luminescence centered at around 700 nm upon irradiation with near-ultraviolet light in crystalline solid and low-temperature glasses. Luminescence was not observed in solution even just above the glass transition temperature in saturated LiCl and 1 *M* HCl. The most significant feature of the luminescence is the remarkable temperature dependence of the quantum yield and lifetime. For the crystalline chloro complex, the quantum yield and lifetime at 8.4 and 290 K were 0.024 and 35 μsec and 0.0013 and 0.71 μsec, respectively. From this temperature dependence, it was concluded that there is a nonemissive state above the emissive excited state (ΔE = 1126, 2256, and 2117 cm^{-1} for the complexes with axial ligands H_2O, Cl^-, and Br^-, respectively). The emissive and nonemissive states are assigned to the $d\sigma^*$ character and are the spin orbit components of the $^3(d\pi^*d\sigma^*)$ configuration. Polycrystalline samples of the sulfate complexes $K_2[Pt_2(SO_4)_4(H_2O)_2]$ and $K_4[Pt_2(SO_4)_4Cl_2]$ also show weak emission at 77 K, with emission maximum at 694 and 755 nm, respectively (*113*). The intensity is much weaker and the lifetime (450 and 290 nsec, respectively) shorter than those of the corresponding phosphate complexes. Emission was not observed at room temperature.

D. ^{195}Pt NMR SPECTRA

^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectra are available in the literature for various lantern-type diplatinum complexes. ^1H, ^{13}C, and ^{31}P NMR spectra have been used mainly for structural assignments and are not useful for comparison among various lantern-type compounds with different bridging ligands.

^{195}Pt NMR data are summarized in Table VI (*24, 25, 48, 55, 116*). The chemical shift spans a fairly wide range that is mainly dependent on the coordination atoms of the bridging ligands. It is seen that the oxidation state has a rather minor influence on the chemical shift as exemplified by the data for the pop complexes. The axial ligands also have only a minor influence on the chemical shift. The complexes with oxygen donor bridging ligands such as sulfate and phosphate give the most positive ^{195}Pt chemical shift. The pop complexes with P as the donor atom resonate at the most negative region. The complexes with

TABLE VI

^{195}Pt NMR CHEMICAL SHIFTS OF SOME QUADRUPLY BRIDGED Pt(II) AND Pt(III) DIMERS IN AQUEOUS MEDIA (vs K_2PtCl_4)

Compounds[a]	δ (ppm)	Reference	Compounds[a]	δ (ppm)	Reference
$[Pt_2(SO_4)_4(Me_2SO)_2]^{2-}$	3394	*116*	$[Pt_2(CH_3COO)_2(CH_2COO)_2Cl_2]^{2-}$	905	*24*
$[Pt_2(SO_4)_4(H_2O)_2]^{2-}$	3382	*116*	$[Pt_2(CH_3COO)_3(CH_2COO)(H_2O)_2]^{+}$	1340, 2753	*25*
$[Pt_2(SO_4)_4Cl_2]^{4-}$	3346	*116*	$[Pt_2(CH_3COO)_3(CH_2COO)Cl_2]^{-}$	1192, 2808	*25*
$[Pt_2(SO_4)_4(NO_2)_2]^{4-}$	3291	*116*	$[Pt_2(CH_3COO)_3(CH_2COO)Br_2]^{-}$	1060, 2768	*25*
$[Pt_2(SO_4)_4(NH_3)_2]^{2-}$	3269	*116*			
$[Pt_2(SO_4)_4(CN)_2]^{4-}$	3228	*116*	*cis*-$[Pt_2(4\text{-mpyt})_4(CN)_2]$	−1890[b]	*48*
$[Pt_2(SO_4)_4Br_2]^{4-}$	3218	*116*	*cis*-$[Pt_2(4\text{-mpyt})_4Cl_2]$	−2066[b]	*48*
$[Pt_2(SO_4)_4(SCN)_2]^{4-}$	3060	*116*	*cis*-$[Pt_2(4\text{-mpyt})_4Br_2]$	−2158[b]	*48*
			cis $[Pt_2(4\text{-mpyt})_4I_2]$	−2306[b]	*48*
$[Pt_2(HPO_4)_4Cl_2]^{4-}$	3448	*116*			
$[Pt_2(HPO_4)_4(Me_2SO)_2]^{2-}$	3435	*116*	$[Pt_2(P_2O_5H_2)_4Cl_2]^{4-}$	−2609	*55*
$[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$	3422	*116*	$[Pt_2(P_2O_5H_2)_4Br_2]^{4-}$	−2918	*55*
$[Pt_2(HPO_4)_4(CN)_2]^{4-}$	3386	*116*	$[Pt_2(P_2O_5H_2)_4I_2]^{4-}$	−3477	*55*
$[Pt_2(HPO_4)_4Br_2]^{4-}$	3370	*116*	$[Pt_2(pcp)_4Cl_2]^{4-}$	−2423	*55*
$[Pt_2(HPO_4)_4(NO_2)_2]^{4-}$	3335	*116*	$[Pt_2(pcp)_4Br_2]^{4-}$	−2672	*55*
$[Pt_2(HPO_4)_4(NH_3)_2]^{2-}$	3279	*116*	$[Pt_2(pcp)_4I_2]^{4-}$	−3123	*55*
$[Pt_2(HPO_4)_4(SCN)_2]^{4-}$	3169	*116*			
			$[Pt_2(pcp)_4]^{4-}$	−3411	*55*
			$[Pt_2(P_2O_5H_2)_4I_2]^{4-}$	−3513	*55*

[a] 4-mpyt, 4-methylpyridine-2-thiolate; pcp, μ-methylenebis(phosphonite) (μ-$CH_2(P(O)OH)_2$).

[b] Measured in $CDCl_3$ (vs H_2PtCl_6).

mixed-donor atoms, including C, N, and S, resonate in the intermediate region.

Some Pt—Pt coupling constant ($^1J_{Pt-Pt}$) data are given in Table VII. The values of the two pop complexes with different oxidation states, $Pt(II)_2$ and $Pt(III)_2$ (*55*), clearly reflect the different extents of

TABLE VII

SOME $^1J_{Pt-Pt}$ VALUES OF LANTERN-TYPE DIPLATINUM COMPLEXES

Compounds	$^1J_{Pt-Pt}$	Reference
$[Pt_2(SO_4)_4(H_2O)Cl]^{3-}$[a]	3464	*116*
$[Pt_2(HPO_4)_4(H_2O)Cl]^{3-}$[b]	5342	*116*
$[Pt_2(P_2O_5H_2)_4]^{4-}$	800	*55*
$[Pt_2(P_2O_5H_2)_4Cl_2]^{4-}$	8080	*55*
$[Pt_2(CH_3COO)_3(CH_2COO)(H_2O)_2]^{+}$	7300	*25*

[a] ^{195}Pt chemical shifts at 3264 and 3435 ppm.

[b] ^{195}Pt chemical shifts at 3339 and 3512 ppm.

metal–metal interaction. However, within the $Pt(III)_2$ complexes, there is no direct correlation between the $^1J_{Pt-Pt}$ value and the Pt—Pt distance (*116*). Thus the complexes with shorter Pt—Pt distances, namely, the sulfate and phosphate complexes, exhibit rather smaller coupling constants. The coupling constant is also the subject to significant axial ligand dependence. Extensive study on the sulfate and phosphate complexes indicated that the coupling constant decreases with the increase in the *trans* influence of the axial ligands. For example, the constants of the sulfate complexes are 703.7 and 3472 ppm for the dicyano and the bromo–aqua complexes, respectively (*116*).

IV. Redox Properties

Before we discuss the redox chemistry of the quadruply bridged diplatinum complexes, relevant structural differences between the $Pt(II)_2$ and the $Pt(III)_2$ states should be noted. First, the Pt—Pt distance is significantly shorter for the $Pt(III)_2$ states due to Pt—Pt single bond formation. Thus the ligands with a shorter bite distance tend to stabilize the $Pt(III)_2$ state. This is consistent with the fact that redox interconversions between the $Pt(II)_2$ and the $Pt(III)_2$ states are possible with ligands having longer bite distances (>ca. 2.7 Å). Second, the $Pt(III)_2$ state usually requires two axial ligands, whereas the $Pt(II)_2$ state has no axial ligand.

Spectrophotomeric study of the voltammetric oxidation of $[Pt_2(pop)_4]^{4-}$ in aqueous phosphate buffer solution in the presence of an excessive amount of various halide anions ($X^- = Cl^-$, Br^-, or I^-) by use of the OTTLE cell technique indicated the quantitative formation of $[Pt_2(pop)_4X_2]^{4-}$ with expected isosbestic points (*128*). The intermediate mixed-valence state was not detected. Cyclic voltammetric study employing similar conditions revealed that the oxidation potential depends significantly on the kind of coexisting halide ions. It was suggested that a small amount of $[Pt_2(pop)_4X]^{5-}$ in equilibrium with $[Pt_2(pop)_4]^{4-}$ in the vicinity of the electrode undergoes oxidation.

Cyclic voltammograms of $[Pt_2(pyt)_4]$ and $[Pt_2(pyt)_4X_2]$ ($X^- = Cl^-$, Br^-, I^-, SCN^-) in DMF are illustrated in Figs. 21 and 22, respectively (*47*). $[Pt_2(pyt)_4]$ undergoes two-electron oxidation with a ligation of solvent molecules at the axial position at +0.282 V vs $Ag/Ag(cryp(2,2))^+$ ($E_{1/2}(Fc^{+/0}) = +0.466$ V).

$$[Pt_2^{II}(pyt)_4] + 2S \rightleftharpoons [Pt_2^{III}(pyt)_4S_2]^{2+} + 2e^-$$

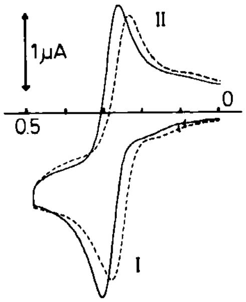


FIG. 21. Cyclic voltammograms of $[Pt_2(pyt)_4]$ (—) and $[Pt_2(4\text{-mpyt})_4]$ (---) in 0.05 *M* TBAP–DMF. (Reprinted with permission from Ref. 47. Copyright © 1987 by American Chemical Society.)

The reduction potentials of complexes $[Pt_2(pyt)_4X_2]$ depend on the kind of axial ligand X^- ($X^- = Cl^-$, -0.44 V; Br^-, -0.32 V; SCN^-, -0.24 V; I^-, -0.23 V). However, the reoxidation potentials of the reduced species are constant ($+0.28$ V) irrespective of the kind of coexisting anions and are the same as the oxidation potential of $[Pt_2(pyt)_4]$. Addition of methanol to the electrolized DMF solution revealed that the solvent-coordinated species is formed first and then the coordinated solvent is rapidly substituted by X^-. The redox processes are schematized as follows.

$$\begin{tikzcd}
\lbrack \mathrm{Pt^{III}}_2(\mathrm{pyt})_4\mathrm{X}_2\rbrack \arrow[r, shift left, "+2e^-"] & \lbrack \mathrm{Pt^{II}}_2(\mathrm{pyt})_4\mathrm{X}_2\rbrack^{2-} \arrow[l, shift left, "-2e^-"] \arrow[d, "-2X^-"] \\
\lbrack \mathrm{Pt^{III}}_2(\mathrm{pyt})_4(\mathrm{S})_2\rbrack \arrow[u, "2X^-"] \arrow[r, shift left, "{+2e^-,\ -2S}"] & \lbrack \mathrm{Pt^{II}}_2(\mathrm{pyt})_4\rbrack \arrow[l, shift left, "{-2e^-,\ +2S}"]
\end{tikzcd}$$

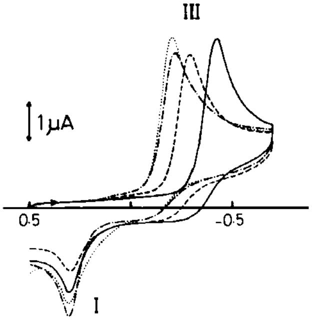


FIG. 22. Cyclic voltammograms of $[Pt_2(pyt)_4X_2]$ in TBAP–DMF, for $X^- = Cl^-$ (—), Br^- (---), I^- (···), and SCN^- (-·-). (Reprinted with permission from Ref. 47. Copyright © 1987 by American Chemical Society.)

The dipalladium complex $[Pd_2(pyt)_4]$ in dichloromethane is irreversibly oxidized at +0.608 V vs Ag/Ag^+ ($E_{1/2}(Fc^{+/0})$ = +0.205 V) (*84*). The redox processes became quasi-reversible in the presence of Cl^- or Br^-, with $E_{1/2}$ values of +0.129 and +0.150 V, respectively (Fig. 23). From a plot of $[Pd_2(pyt)_4]/[X^-]$ against oxidation current, it was concluded that one X^- per complex is involved in the redox process. However, the redox process is likely to be a two-electron one on the basis of the ΔE_p value.

$$[Pd_2(pyt)_4] + X^- \rightleftharpoons [Pd_2(pyt)_4X]^+ + 2e^-$$

In contrast to $[Pd_2(pyt)_4]$, $[Pd_2(form)_4]$ exhibits two reversible one-electron oxidation processes in dichloromethane ($E_{1/2}$ = +0.81 and +1.19 V vs Ag/AgCl ($E_{1/2}(Fc^{+/0})$ = +0.49 V)) (Fig. 24) (*78, 79*). In this case, the oxidation occurs at the ligand site at least in the first oxidation step. However, $[Ni_2(form)_4]$ exhibits a reversible oxidation and an irreversible oxidation process in dichloromethane at $E_{1/2}$ = +0.73 V and E_{pa} = +1.25 V, respectively. It is worth noting that the *form* complexes do not require axial ligands in their oxidation processes.

$$[Pd_2(form)_4] \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} [Pd_2(form)_4]^+ \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} [Pd_2(form)_4]^{2+}$$

$$[Ni_2(form)_4] \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} [Ni_2(form)_4]^+ \xrightarrow{-e^-} [Ni_2(form)_4]^{2+} \xrightarrow{-e^-} \text{decompose}$$

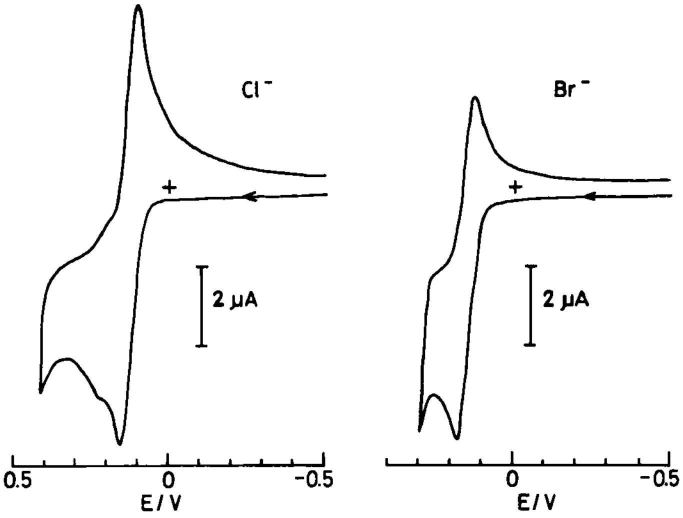


FIG. 23. Cyclic voltammograms of $[Pd_2(pyt)_4]$ in the presence of 0.01 *M* Bu_4NCl (left) and 0.01 *M* Bu_4NBr (right) in 0.1 *M* TBAP–CH_2Cl_2. (Reprinted with permission from Ref. 84. Copyright © 1990 by American Chemical Society.)

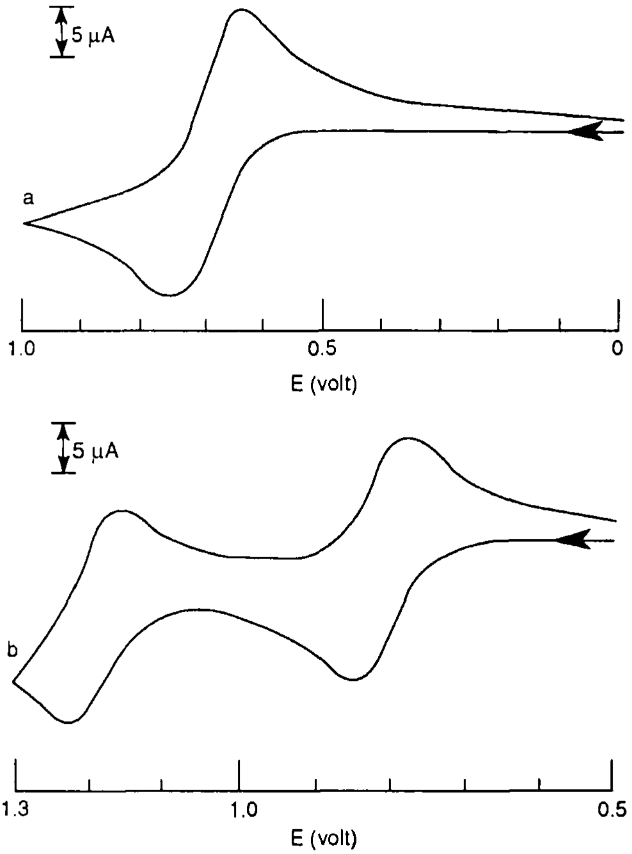


FIG. 24. Cyclic voltammograms of $M_2(form)_4$ in CH_2Cl_2 (ca. 0.1 *M* Bu_4NPF_6) at a platinum electrode: (a) M = Ni; (b) M = Pd. (Reprinted with permission from Ref. 78. Copyright © 1987 by American Chemical Society.)

$[Pd_2(dpb)_4]$ exhibits a reversible oxidation process at +0.65 V vs SCE in dichloromethane (*80*). The EPR measurement at 123 K of the oxidized species at +0.7 V indicates that the electron was removed from the metal-centered molecular orbital and an odd electron exists in the M—M σ^* orbital.

V. Axial Ligand Substitution Properties

Axial ligands of the quadruply bridged Pt(III) complexes are known to be easily replaced by other donor ligands. This property has been used for the preparation of a variety of diplatinum(III) complexes with different axial ligands (*18, 21*). Kinetic studies were reported for some axial ligand substitution reactions (*25, 126, 129, 130*). Available data on the following anation reactions are given in Table VIII.

$$[Pt_2(L)_4(H_2O)_2]^{n-} + X^- \longrightarrow [Pt_2(L)_4(H_2O)X]^{m-} + Y^- \longrightarrow [Pt_2(L)_4XY]^{p-}$$

The following behavior appears to be difficult to explain at the moment. First, although the initial and second halide substitutions for the diaqua complexes proceed with similar rate constants for the HPO_4^{2-} complex, the first step for the SO_4^{2-} complex is rapid (*17*), and only the slower second step has been studied kinetically (*130*). These two complexes are similar in many respects as described in other sections. Second, although the labile nature is attributed to the strong metal–metal bonding, the pop complex with a much longer Pt—Pt distance gives a substitution rate constant (for the chloro–aqua to dichloro conversion), falling between those of the other two complexes with much shorter Pt—Pt distances. It should be noted, however, that since these rate constants appear to be pH dependent, direct comparisons in Table VIII should be made with care.

The axial halide exchange reactions were also studied (*126*).

$$[Pt_2(pop)_4X_2]^{4-} + Y^- \longrightarrow [Pt_2(pop)_4XY]^{4-} + X^-$$

These reactions are catalyzed by the addition of the corresponding Pt(II) dimer, $[Pt_2(pop)_4]^{4-}$, which has no axial ligand, and are also photocatalyzed. The $Pt_2—X—Pt_2$ type of intermediate has been postulated for the Pt(II)-catalyzed pathway. It should be noted that the anation reaction is not catalyzed by the Pt(II) dimer.

In the asymmetrical complex $[Pt_2(CH_3COO)_3(CH_2COO)(H_2O)_2]^-$, the $Pt(O)_4$ site undergoes rapid substitution followed by slower (by at least one order of magnitude) substitution at the $Pt(O)_3C$ site with a Pt—C bond from CH_2COO^{2-} (*25*). This is consistent with the shorter $Pt—OH_2$ bond distance at the $Pt(O)_3C$ center (2.43 vs 2.46 Å). The very short Pt—C bond does not result in a long $Pt—OH_2$ distance at the *cis*-position. As to the mechanism of axial ligand substitution, an interchange mechanism has been suggested on the basis of the highly negtive $\Delta S^{\neq}$ values for the substitutions of the pop complex (*126*). The only information available as to the lability of bridging ligands is that the tetra(acetato) Pt(III) complex easily dissociates one of the acetates. This is the result of the highly strained structure caused by the coordination of the quadruply bridged ligands and the short bite distance (*30*).

TABLE VIII

RATE AND EQUILIBRIUM CONSTANT DATA FOR AXIAL LIGAND SUBSTITUTION REACTIONS IN AQUEOUS SOLUTIONS

BL	X^-	Y^-	pH	I (M)	k_1 (M^{-1} sec^{-1})	k_{-1} (sec^{-1})	k_2 (M^{-1} sec^{-1})	k_{-2} (sec^{-1})	K_1 (M^{-1})	K_2 (M^{-1})	Reference
HPO_4^{2-}	Cl^-	Cl^-	3.0	0.1 (phosphate)	0.9	5×10^{-2}	0.8	8×10^{-2}	19	11	*129*
	Br^-	Br^-	3.0	0.1 (phosphate)	0.3	1.5×10^{-2}	0.4	1.9×10^{-2}	21	22	*129*
$P_2O_5H_2^{2-}$	Cl^-	Cl^-	3.8	0.055 ($NaClO_4$–$HClO_4$)	—	—	0.08[a]	—	—	—	*130*
	Br^-	Cl^-	3.8	0.055 ($NaClO_4$–$HClO_4$)	—	—	0.27[b]	—	—	—	*130*
	Br^-	Br^-	3.4	0.055 ($NaClO_4$–$HClO_4$)	—	—	0.37	—	—	—	*130*
	Br^-	Br^-	—	0.05 M $HClO_4$	—	—	0.34	—	—	—	*130*
	Br^-	Br^-	7.6	0.055 ($NaClO_4$–$HClO_4$)	—	—	2.84	—	—	—	*130*
	Br^-	SCN^-	4.0	0.055 ($NaClO_4$–$HClO_4$)	—	—	2.8	—	—	—	*130*
	Cl^-	Cl^-	—	—	—	—	—	8.9×10^{-6}	—	—	*126*
SO_4^{2-}	Cl^-	Cl^-	—	0.5 M $HClO_4$	Rapid	—	0.016	—	—	—	*130*

Note. $[Pt_2(BL)_4(H_2O)_2]^{2-} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt_2(BL)_4X(H_2O)]^{3-} + Y^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Pt_2(BL)_4XY]^{4-}$.

[a] $\Delta H^{\neq} = 39$ kJ mol^{-1}; $\Delta S^{\neq} = -135$ J K^{-1} mol^{-1}.

[b] $\Delta H^{\neq} = 38$ kJ mol^{-1}; $\Delta S^{\neq} = -140$ J K^{-1} mol^{-1}.

VI. Concluding Remarks

In this chapter we have tried to summarize the current status of the chemistry of quadruply bridged dimetal complexes of the group 10 elements. The area is closely related to that involving similar compounds of the group 9 elements and also the doubly bridged di- and polynuclear complexes of platinum and related metals, which are not included here. We have been able to include the latest developments in this subject area. We have not attempted to be comprehensive, and some omissions may have resulted.

ACKNOWLEDGMENTS

We are grateful to Professor S. Ooi and Dr. I. Kinoshita of Osaka City University, Japan, and Professor T. G. Appleton, University of Queensland, Australia, for providing us with their results prior to publication. Financial support by a Grant-in-Aid for Scientific Research on Priority Area (No. 03231105) from the Ministry of Education, Science, and Culture, Japan, is gratefully acknowledged.

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