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Palladium(II) and Platinum(II) Complexes with 1,5-Dithiacyclooctane (dtco): Structures of $[Pd(dtco)Cl_2]$ and $[Pd(dtco)_2](NO_3)_2$ and Kinetics of Ligand Substitution in $[Pd(dtco)_2]^{2+}$ by Bidentate Ligands

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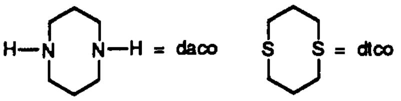
Complex formation of divalent transition metals with the cyclic dithioether dtco = 1,5-dithiacyclooctane was studied, and the complexes $[Pd(dtco)Cl_2]$, $[Pt(dtco)Cl_2]$, and $[Pd(dtco)_2](NO_3)_2$ were prepared and characterized. It follows from conductivity measurements that in water $[Pd(dtco)Cl_2]$ dissociates partially and $[Pd(dtco)_2](NO_3)_2$ dissociates completely. Both complexes are diamagnetic. X-ray structure analysis confirms square-planar coordination geometry around the palladium for both $[Pd(dtco)Cl_2]$ (monoclinic; space group $P2_1/c$; $a = 6.583$ (2) Å, $b = 12.489$ (3) Å, $c = 13.429$ (3) Å, $\beta = 113.32$ (1)°; $Z = 4$; $R(F_o) = 0.0274$) with a S_2Cl_2 set of donor atoms and $[Pd(dtco)_2](NO_3)_2$ (monoclinic; space group $2/m$; $a = 9.970$ (4) Å, $b = 12.793$ (5) Å, $c = 7.350$ (3) Å, $\beta = 91.49$ (1)°; $Z = 2$; $R(F_o) = 0.0253$) with a S_4 set of donor atoms, the dtco ligands being coordinated in a folded, "butterfly-like" form (boat–chair conformation). The two nitrate ions in the $(dtco)_2$ complex are located perpendicularly to the PdS_4 coordination plane, each one bridging two Pd atoms. Stopped-flow spectrophotometry was used to study the kinetics of ligand substitution in $[Pd(dtco)_2]^{2+}$ by bidentate ligands L-L = bpy (2,2′-bipyridine) and phen (1,10-phenanthroline) in $MeOH/H_2O$ (9:1) under pseudo-first-order conditions ($[L\text{-}L] \geq 10[Pd(dtco)_2{}^{2+}]$) at 293 K and $I = 0.1$ M ($NaNO_3$). The reactions lead to the mixed ligand species $[Pd(dtco)(L\text{-}L)]^{2+}$ and follow a second-order rate law, rate = $k[L\text{-}L][Pd(dtco)_2{}^{2+}]$, with $k_{bpy} = 20.0 \pm 0.2$ and $k_{phen} = 70.2 \pm 2.1$ M^{-1} s^{-1}. For L-L = bpy, the activation parameters are $\Delta H^* = 9.46 \pm 0.44$ kcal mol^{-1} and $\Delta S^* = -32.2 \pm 1.40$ cal K^{-1} mol^{-1}. The kinetic results support the operation of an associative (A) mechanism. The reaction of $[Pd(dtco)_2]^{2+}$ with L-L = mnt^{2-} (dianion of dimercaptomaleonitrile) is a two-step process leading to the intermediate $[Pd(dtco)(mnt)]$ ($k > 2 \times 10^5$ M^{-1} s^{-1}), which is converted to the product $[Pd(mnt)_2]^{2-}$ in a consecutive second-order reaction ($k = 14.5 \pm 0.2$ M^{-1} s^{-1}). The structural and kinetic results are discussed in comparison to corresponding complexes with the diaza ligand daco = 1,5-diazacyclooctane.

Introduction

The eight-membered heterocycles 1,5-diazacyclooctane = daco and 1,5-dithiacyclooctane = dtco are too small to fulfill the formal conditions[1] required for so-called macrocyclic ligands. To become coordinated as bidentate ligands, daco and dtco have to adopt a folded, butterfly-like conformation, the "cavity" offered by these cyclic molecules with two donor atoms being too small for accommodating a transition-metal cation. In contrast to linear bidentate N_2 ligands such as ethylenediamine the folded conformation of daco and dtco creates so much steric crowding that only two of these ligands are coordinated by transition-metal cations.



$[Cu(daco)_2]^{2+}$ and $[Ni(daco)_2]^{2+}$, first described by Musker and Hussain,[2] are complex species with a planar N_4 coordination geometry. As shown by Billo[3] and confirmed by Hay et al.,[4] the rate of acid dissociation of the diamagnetic cation $[Ni(daco)_2]^{2+}$ in dilute $HClO_4$ is surprisingly small. This exceptional kinetic inertness was ascribed to the specific conformational arrangement of the propylene bridges connecting the nitrogen atoms in the coordinated ligands,[2,5,6] which provides shielding of the axial sites. We have shown recently[7] that the corresponding copper(II) complex, $[Cu(daco)_2]^{2+}$, is labile instead and dissociates readily in acidic medium.

The coordination chemistry of cyclic thioethers can differ significantly from the coordination chemistry of the corresponding aza macrocycles.[8] It is not really surprising therefore that the complex $[Ni(dtco)_2](ClO_4)_2$, which was first prepared by Musker and Hill[9] and which represents the "sulfur analogue" of the kinetically inert complex $[Ni(daco)_2](ClO_4)_2 \cdot 2H_2O$, is thermodynamically not very stable and dissolves in nitromethane or acetone with loss of the thioether ligand.

In continuation of our work on the kinetic behavior of four-coordinate complexes with d^8 (Pt(II),[10] Pd(II),[11] Ni(II)[11,12]) and d^9 metal centers (Cu(II)[13]), we decided to further study complex formation with the sulfur donor ligand dtco, aim for sufficiently stable four-coordinate dtco complexes $[M(dtco)_2]^{2+}$ ($M = Pd^{2+}$, Pt^{2+}) and investigate their kinetic behavior in ligand substitution according to (1) (L-L = bidentate ligand). One goal of the present

$$[M(dtco)_2]^{2+} + 2L\text{-}L \rightleftharpoons [M(L\text{-}L)_2]^{2+} + 2dtco \tag{1}$$

contribution was thus to provide further information on the properties and reactivity of transition-metal complexes with the cyclic dithia ligand dtco, to allow for a comparison with the complexes formed with the corresponding diaza ligand daco.

Experimental Section

The solvent methanol (Merck) as well as the chemicals Cs_2CO_3 (Alfa), 2,2′-bipyridyl (bpy), and 1,10-phenanthroline monohydrate ($phen \cdot H_2O$) (both from Janssen Chimica) were reagent grade and were used without further purification. $PdCl_2$ and $PtCl_2$ (both 99%) were a loan from Degussa AG. The ligands dtco[14] (from 1,3-diiodopropane, Aldrich, and 1,3-dimercaptopropane, Fluka) and $Na_2(mnt)$ (disodium dimercaptomaleonitrile)[15] as well as the complexes *trans*-$[Pd(BN)_2Cl_2]$

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(*trans*-bis(benzonitrile)dichloropalladium(II)[16]), $[Pd(bpy)_2](NO_3)_2$,[17] and $(Et_4N)_2[Pd(mnt)_2]$[18] were prepared according to published procedures.

Complexes. $[Pt(dtco)Cl_2]$ was prepared by dissolving 3 mmol of $PtCl_2$ in 25 mL of DMSO at 80 °C under stirring and by adding dropwise a solution of 6 mmol of the ligand dtco in very little DMSO. Within a few minutes, a yellow precipitate formed, which, after cooling of the solution, was filtered, washed with acetone and dimethyl ether, and dried in vacuo to give yellow crystals, yield 68%, mp > 260 °C dec. Anal. Calcd: C, 17.38; H, 2.90; Cl, 17.1. Found: C, 17.42; H, 2.81; Cl, 16.7.

$[Pd(dtco)Cl_2]$ was obtained by adding 2 mmol of the ligand dtco to a filtered solution of 1.8 mmol of *trans*-$[Pd(BN)_2Cl_2]$ in 30 mL of benzene. The yellow complex precipitated immediately and was filtered, washed with acetone and ether, and dried in vacuo (yield 70%). Slow recrystallization from nitromethane led to large orange crystals, mp > 250 °C dec. Anal. Calcd: C, 22.13; H, 3.69; Cl, 21.8. Found: C, 22.38; H, 3.73; Cl, 19.8. The complex can also be recrystallized from water.

$[Pd(dtco)_2](NO_3)_2$ was prepared by fist adding 3.4 mmol of the ligand dtco to a solution of 1.68 mmol of $PdCl_2$ in 60 mL of DMSO at 100 °C under stirring. The color changed immediately from red to yellow. Addition of a solution of 3.4 mmol of $AgNO_3$ in 20 mL of DMSO led to a precipitate of AgCl, which was separated by filtration. Partial removal of the solvent DMSO by distillation in vacuo produced a more concentrated filtrate from which the complex crystallized upon cooling. The product (yield 56%) was filtered, washed with acetone and ether, and dried for 10 h at 100 °C in vacuo. Recrystallization from DMSO/acetone gave yellow crystals of $[Pd(dtco)_2](NO_3)_2$, mp > 190 °C dec. Anal. Calcd: C, 27.32; H, 4.55; N, 5.31. Found: C, 27.38; H, 4.53; N, 5.12.

Instrumentation. UV/vis spectra, diode array spectrophotometer (Hewlett-Packard 8451 A), quartz cells; magnetic susceptibility, Gouy-type magnetic balance (Johnson Matthey Chemicals); conductivity, conductometer (Metrohm, E 365 E), Pt electrode.

X-ray Structure Determination. The crystals of $[Pd(dtco)Cl_2]$ (size 0.15 × 0.37 × 1.3 mm) and of $[Pd(dtco)_2](NO_3)_2$ (size 0.075 × 0.125 × 0.225 mm) were grown from water and methanol, respectively. Intensities were measured with a four-cycle diffractometer (Stoe-Siemens AED 2) using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Cell constants were determined by least-squares methods from the 2θ angles of 56 and 62 reflections, respectively, measured on the same instrument.

Lp (Lorentz–polarization) and background corrections were applied. Absorption was corrected numerically ($[Pd(dtco)Cl_2]$; SHELX76) and empirically ($[Pd(dtco)_2](NO_3)_2$; control program of the diffractometer). The structure of $[Pd(dtco)Cl_2]$ was solved by SHELXS86. Since there are only two formula units $[Pd(dtco)_2](NO_3)_2$ in the unit cell of space group *C*2/*m* the asymmetric unit is formed by one-quarter of a complex cation and half of a nitrate anion and the Pd must occupy a special position of symmetry 2/*m*. It was placed in 0, 0, 0. The position of the S was obtained from a Patterson synthesis; the rest of the structure was found from Fourier syntheses. The structures were refined to the *R* values given in Table III. Hydrogen atoms were positioned geometrically (C–H distance 1.08 Å) and not refined. An extinction correction was applied. All crystallographic calculations were performed with the program SHELX76 on a Micro-VAX II computer at Stoe & Cie, Darmstadt, Germany. Scattering factors for C, H, N, O, and Cl are stored in SHELX76.[19] The final positional parameters are given in Table IV.

Kinetic Measurements. Reactions 1 were followed with a modified[13a] stopped-flow spectrophotometer (Durrum, Model D 110). Pseudo-first-order conditions were maintained ($[L\text{-}L]_0 \geq 10[\text{complex}]_0$) and the absorbance/time data were computer-fitted to eq 2 with a program based

$$A = (A_0 - A_\infty)\exp(-k_{obsd}t) + A_\infty \quad (2)$$

on the least-squares method (*A* = absorbance). The complete set of data obtained for the experimental rate constant k_{obsd} is available as supplementary material (Table SV).

Results and Discussion

Preparation and Properties of the Complexes. The reaction of $PtCl_2$ with the ligand dtco in DMSO in a molar ratio of 1:2 leads to the product $[Pt(dtco)Cl_2]$, which means that the bidentate ligand cannot compete with the two chloride ions to form the $(dtco)_2$ complex $[Pt(dtco)_2]Cl_2$. The analogous reaction of $PdCl_2$ with dtco affords the complex $[Pd(dtco)Cl_2]$. The product is not pure, however, and is hard to purify. The better route to $[Pd(dtco)Cl_2]$ is the reaction of *trans*-$[Pd(BN)_2Cl_2]$ with dtco, as described in the Experimental Section. Removal of the chloride ions from $[Pd(dtco)Cl_2]$ with silver nitrate (precipitation of AgCl) in the presence of dtco leads to the bis complex $[Pd(dtco)_2](NO_3)_2$. Copper(II) complexes such as $[Cu(dtco)X_2]$ (X = halide) or $[Cu(dtco)_2]Y_2$ (Y = perchlorate) could not be obtained due to rapid oxidation of dtco by copper(II).[20] The reaction of copper(I) chloride with dtco (CuCl:dtco = 1:2) in DMSO at 80 °C afforded a colorless solid of the composition Cu:dtco:Cl = 1:1:1. The extremely low solubility of this product in common solvents suggests, however, that it has a polymeric structure $[Cu(dtco)Cl]_x$.

Table I. Molar Conductivity of Complexes $[Pd(dtco)Cl_2]$ and $[Pd(dtco)_2](NO_3)_2$ in Water and Dimethyl Sulfoxide

complex	solvent	Λ_m, Ω^{-1} cm^2 mol^{-1} [a]
$[Pd(dtco)Cl_2]$	H_2O	86
	DMSO	1.2
$[Pd(dtco)_2](NO_3)_2$	H_2O	196
	DMSO	66
1:1 electrolytes[a,b]	DMF	65–90
	nitromethane	75–95
2:1 electrolytes[a,b]	DMF	130–170
	nitromethane	150–180

[a] At [complex] = 10^{-3} M and 25 °C. [b] From: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table II. UV/Vis Absorption and Magnetic Moments of the Complexes

complex	solvent	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	μ_{eff}, μ_B [a]
$[Pd(dtco)Cl_2]$	H_2O	204	11400	0
		232	8400	
		290	9750	
		376	1050 (sh)	
$[Pd(dtco)_2](NO_3)_2$	H_2O	208	16400	0
		256	9700	
		334	19100	
	$MeOH/H_2O$[b]	258	11400	
		334	20100	
$[Pt(dtco)Cl_2]$	DMSO	264	2660	0
		316	716	
$[Pd(bpy)_2](NO_3)_2$	$MeOH/H_2O$[b]	254	21700	
		314	18500	
$[Pd(dtco)(bpy)]^{2+}$[c]	$MeOH/H_2O$[b]	278	18900	
		312	12400	
		322	12800	
$(Et_4N)_2[Pd(mnt)_2]$[d]	$MeOH/H_2O$[b]	436	5700	
		638	60	

[a] From susceptibility data taken for the solid complex at 25 °C. [b] MeOH:H_2O = 9:1. [c] Data obtained for a solution of $[Pd(dtco)_2](NO_3)_2$ and bpy (1:1) after it was allowed to stand at ambient temperature. [d] UV absorptions omitted.

It follows from the conductivity data compiled in Table I that $[Pd(dtco)Cl_2]$ dissociates partially in water, but not in dimethyl sulfoxide (DMSO). The molar conductivity measured in water suggests formation of the species $[Pd(dtco)Cl(H_2O)]^+$ according to (3). The fact that the complex can be recrystallized from water confirms the reversibility of this aquation reaction.

$$[Pd(dtco)Cl_2] + H_2O \rightleftharpoons [Pd(dtco)Cl(H_2O)]^+ + Cl^- \quad (3)$$

The complex $[Pd(dtco)_2](NO_3)_2$ ionizes in water and behaves like a 1:2 electrolyte (see Table I). The conductivity found in the solvent DMSO, however, suggests only partial ionization and formation of species such as $[Pd(dtco)_2]NO_3^+$, if one compares the observed value of Λ_m = 66 with those typically obtained for 1:1 and 2:1 electrolytes in strongly polar aprotic solvents such as dimethylformamide (DMF) and nitromethane (see Table I).

As is to be expected, the three novel dtco complexes of Pd(II) and Pt(II) prepared are diamagnetic (μ_{eff} = 0; see Table II). The

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Table III. Crystallographic Data for Complexes [Pd(dtco)Cl$_2$] and [Pd(dtco)$_2$](NO$_3$)$_2$

[Pd(dtco)]Cl$_2$	[Pd(dtco)$_2$](NO$_3$)$_2$
$C_6H_{12}Cl_2PdS_2$	$C_{12}H_{24}N_2O_6PdS_4$
fw = 325.61	fw = 526.99
space group: $P2_1/c$	space group: $C2/m$
a = 6.583 (2) Å	a = 9.970 (4) Å
b = 12.489 (3) Å	b = 12.793 (5) Å
c = 13.429 (3) Å	c = 7.350 (3) Å
β = 113.32 (1)	β = 91.49 (1)
V = 1014 Å^3	V = 937 Å^3
Z = 4	Z = 2
T = 24 °C	T = 25 °C
λ = 0.71069 Å	λ = 0.71069 Å
ρ(calcd) = 2.13 g cm^{-3}	ρ(calcd) = 1.87 g cm^{-3}
μ = 26.09 cm^{-1}	μ = 14.35 cm^{-1}
transm coeff = 0.401–0.616	transm coeff = 0.772–0.861
$R(F_o)$ = 0.0274	$R(F_o)$ = 0.0253
$R_w(F_o)$ = 0.0286	$R_w(F_o)$ = 0.0231

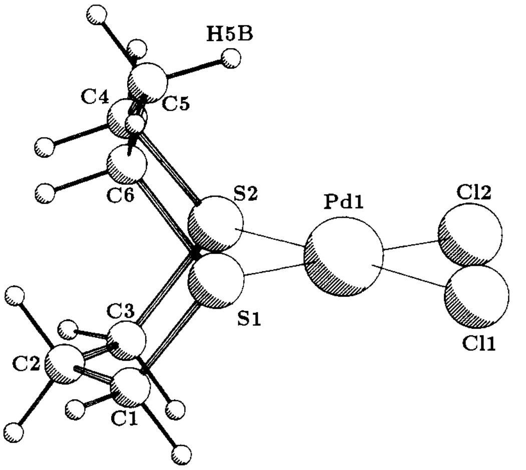

Figure 1. View of the coordination geometry in the complex [Pd(dtco)Cl$_2$].

intense UV absorptions at 204 and 232 nm for [Pd(dtco)Cl$_2$] and at 208 and 256 nm for [Pd(dtco)$_2$](NO$_3$)$_2$ are probably characteristic ligand bands, whereas the strong absorptions at 290 and 334 nm, respectively, can be attributed to LM charge transfer, since the absorption coefficient found for the (dtco)$_2$ complex of palladium(II) is nearly twice as high as that for the mono complex. The shoulder observed for the complex [Pd(dtco)Cl$_2$] at 376 nm is difficult to assign since the conductivity data point to partial hydrolysis of the complex in water. It is important to note that the spectrum of the complex [Pd(dtco)$_2$](NO$_3$)$_2$ in the solvent mixture MeOH/H$_2$O (9:1) is practically identical with that in water (see Table II). This finding implies complete ionization in the solvent mixture MeOH/H$_2$O, which was used for the kinetic studies.

It follows from the spectral data listed in Table II that the reaction of [Pd(dtco)$_2$]$^{2+}$ with bpy should be easy to trace by monitoring the decrease in absorbance at 334 nm, whereas the reaction with the mnt^{2-} ion should be clearly observable at 530 nm.

Structure of the Complexes [Pd(dtco)Cl$_2$] and [Pd(dtco)$_2$](NO$_3$)$_2$. The structure of both complexes could be refined to a high degree of accuracy (see Table III). The unit cells are both monoclinic and contain four and two molecular units, respectively.

Table IV. Atomic Parameters (×10^4) for Complexes [Pd(dtco)Cl$_2$] and [Pd(dtco)$_2$](NO$_3$)$_2$

atom	x	y	z
	[Pd(dtco)Cl$_2$]		
Pd(1)	3042 (0)	8555 (0)	2884 (0)
Cl(1)	1716 (2)	9780 (1)	3795 (1)
Cl(2)	907 (2)	9302 (1)	1214 (1)
S(1)	5227 (2)	7820 (1)	4498 (1)
C(1)	8035 (7)	7965 (3)	4562 (3)
C(2)	8632 (7)	7335 (3)	3764 (3)
C(3)	7399 (8)	7607 (3)	2578 (4)
S(2)	4399 (2)	7417 (1)	1986 (1)
C(4)	4129 (7)	6047 (3)	2390 (3)
C(5)	3313 (8)	5942 (3)	3295 (4)
H(5B)	1756 (8)	6362 (3)	3044 (4)
C(6)	4805 (8)	6369 (3)	4399 (3)
	[Pd(dtco)$_2$](NO$_3$)$_2$		
Pd(1)	0.0	0.0	0.0
S(1)	1631 (1)	1293 (1)	−91 (1)
C(1)	2579 (3)	1006 (3)	−2106 (5)
C(2)	2380 (5)	0.0	−2095 (6)
C(3)	2821 (3)	1023 (2)	1771 (5)
C(4)	2614 (5)	0.0	2784 (6)
H(4A)	1670 (44)	0.0	3321 (58)
N(1)	0.0	2377 (3)	5000
O(1)	0.0	3357 (3)	5000
O(2)	328 (3)	1963 (3)	3657 (5)

Table V. Selected Distances (Å) and Bond Angles (deg) in Complexes [Pd(dtco)]Cl$_2$ and [Pd(dtco)$_2$](NO$_3$)$_2$

[Pd(dtco)]Cl$_2$		[Pd(dtco)$_2$](NO$_3$)$_2$	
Cl(1)–Pd–Cl(2)	92.0 (0)	C(1)–S(1)–Pd	150.0 (1)
Cl(1)–Pd–S(1)	89.5 (0)	C(3)–S(1)–Pd	106.6 (1)
Cl(2)–Pd–S(1)	178.0 (0)	C(3)–S(1)–C(1)	103.4 (2)
Cl(1)–Pd–S(2)	177.8 (0)	S(1)–Pd–S(1)′	90.9 (0)
Cl(2)–Pd–S(2)	87.3 (0)	S(1)–Pd–S(1)″	89.1 (0)
S(1)–Pd–S(2)	91.2 (0)	C(1)–C(2)–C(1)′	116.4 (4)
Pd–S(1)–C(1)	104.6 (1)	C(4)–C(3)–S(1)	115.9 (3)
Pd–S(1)–C(6)	108.1 (1)	C(3)–C(4)–C(3)′	118.5 (4)
C(1)–S(1)–C(6)	102.9 (2)	O(2)–N(1)–O(1)	116.8 (3)
S(1)–C(1)–C(2)	117.4 (3)	O(2)–N(1)–O(2)	126.4 (5)
C(1)–C(2)–C(3)	116.8 (3)	O(2)–Pd–O(2)[a]	85.9 (1)
C(2)–C(3)–S(2)	117.7 (3)	O(2)–Pd–O(2)[b]	94.1 (1)
Pd–S(2)–C(3)	105.9 (1)		
Pd–S(2)–C(4)	108.9 (1)	Pd–S(1)	2.321 (1)
C(3)–S(2)–C(4)	102.0 (2)	S(1)–C(1)	1.816 (3)
S(2)–C(4)–C(5)	115.3 (3)	S(1)–C(3)	1.821 (3)
C(4)–C(5)–C(6)	117.1 (4)	C(2)–C(1)	1.514 (4)
S(1)–C(6)–C(5)	116.2 (3)	C(4)–C(3)	1.522 (4)
		O(1)–N(1)	1.254 (5)
Pd–Cl(1)	2.333 (1)	O(2)–N(1)	1.174 (3)
Pd–S(1)	2.267 (1)	O(2)–Pd	3.687 (2)
Pd–S(2)	2.264 (1)	S(1)–S(1)′	3.308 (2)
Pd–Cl(2)	2.320 (1)	S(1)–S(1)″	3.258 (2)
S(1)–C(1)	1.826 (4)	S(1)–O(2)	3.340 (3)
S(1)–C(6)	1.829 (4)		3.193 (3)
C(2)–C(1)	1.502 (5)		
C(2)–C(3)	1.513 (6)		
C(3)–S(2)	1.829 (5)		
C(4)–S(2)	1.825 (4)		
C(4)–C(5)	1.516 (6)		
C(5)–C(6)	1.515 (6)		
S(1)–S(2)	3.236 (2)		

[a] O–Pd–O angle formed by nitrate oxygens located on the same side of the PdS$_4$ plane. [b] O–Pd–O angle formed by nitrate oxygens located on opposite sides of the PdS$_4$ plane.

The view of the coordination geometry in [Pd(dtco)Cl$_2$] shown in Figure 1 was chosen to demonstrate the planar arrangement of the four donor atoms around the palladium, which is confirmed by the corresponding angles (see Table V). The two Pd–Cl distances are equal within the limits of error, and so are the two Pd–S distances. The cyclic ligand dtco is folded in a butterfly-like fashion in such a way that the middle carbon atom of one propylene bridge (C(2)) is pointing away from the metal whereas the other one (C(5)) is pointing toward it. As a consequence of this one of the H atoms on C(5), labeled as H(5B) in Figure 1, is getting close to one of the vacant axial positions of the palladium. Packing of the four [Pd(dtco)Cl$_2$] molecules within the unit cell is such that there are no interactions among them. The skeleton of the dtco ligand adopts a boat–chair conformation, which is one of the energetically favored conformations.[21a] The four C–S

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(21) (a) Setzer, W. N.; Coleman, B. R.; Wilson, G. S.; Glass, R. S. *Tetrahedron* **1981**, *37*, 2743. (b) Setzer, W. N.; Wilson, G. S.; Glass, R. S. *Tetrahedron* **1981**, *37*, 2735.

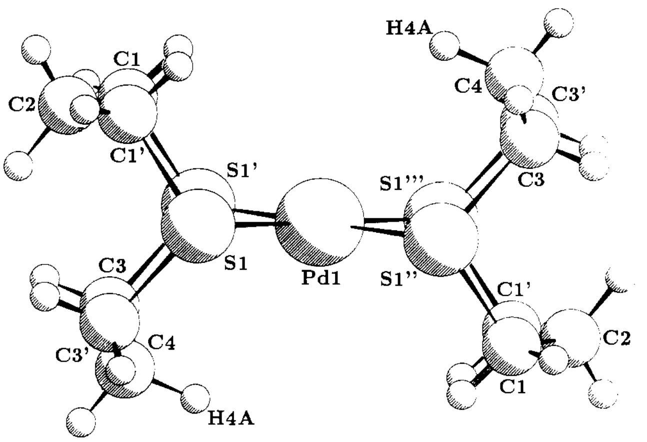


Figure 2. View of the coordination geometry in the complex [Pd(dtco)$_2$](NO$_3$)$_2$.

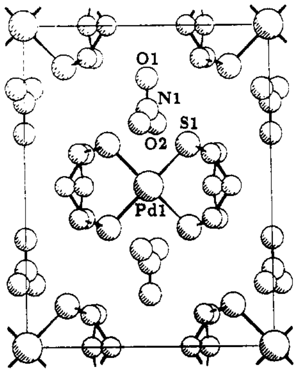
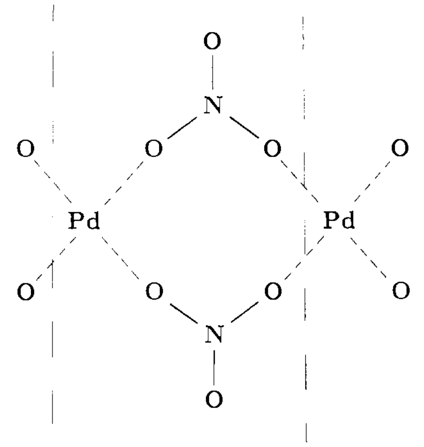


Figure 3. View of the unit cell of the complex [Pd(dtco)$_2$](NO$_3$)$_2$ projected along [001].

distances are practically equal, and so are the C–C distances. The comparison with noncoordinated 1,4-dithiacycloheptane[21b] and 1,5-dithiacyclononane[21b] reveals, however, that the mean C–C distance in the eight-membered coordinated heterocycle dtco is clearly shorter.

The structure of the complex [Pd(dtco)$_2$](NO$_3$)$_2$, in many ways very similar to that of the mono complex [Pd(dtco)Cl$_2$], shows some interesting symmetry properties. The complex occupies a position of symmetry $2/m$, with the mirror plane going through the atoms Pd(1), C(2), and C(4) (see Figure 2). It follows from this symmetry that the coordination of the sulfur atoms around the palladium is strictly planar, with four identical Pd–S distances. The Pd–S distance is, by 0.05 Å, longer than in the mono complex (see Table V), which points to a somewhat weaker Pd–S bond in the bis complex. The C–C and C–S distances and the angles within the coordinated ligands are very similar in both the mono and bis complex (see Table V), the trans annular S–S distance in the bis complex being a little longer (3.308 as compared to 3.236 Å). Both dtco ligands in [Pd(dtco)$_2$](NO$_3$)$_2$ are in the boat–chair conformation (see Figure 2) but the symmetry requires that the hydrogen atoms H(4A), which point toward the axial positions of the palladium, are on opposite sides of the PdS$_4$ coordination plane. The two nitrate ions of each complex unit of [Pd(dtco)$_2$](NO$_3$)$_2$ are located on a 2-fold axis at $z = {}^1/_2$, halfway between two Pd atoms (see Figure 3). The planes of the nitrate ions are oriented perpendicularly to the PdS$_4$ planes in such a way that each NO$_3^-$ ion bridges two Pd atoms according to Chart I, thus forming chains along the z axis. Interestingly, the N–O distance of the two equivalently "coordinated" oxygen atoms is clearly shortened as compared to the N–O distance of the "noncoordinated" O atoms of the nitrate ion (1.174 vs 1.254 Å; see Table V). In addition, the O–N–O angle on the "coordinated" side of the nitrate ion has expanded from 120 to 126.4°. The angles between the bridging nitrate oxygen atoms and the Pd in the PdS$_4$ plane amount to 85.87 and 94.13°, respectively (see Table V). In spite of the large Pd–O distance of 3.687 Å, all these facts concerning the highly symmetrical bridging position of the nitrate ions point to the existence of a considerably strong interaction, which produces a very peculiar type of "pseudo-eight-coordinate" palladium(II).

Chart I. Schematic Representation of the Bridging Function of the Nitrate Ions in [Pd(dtco)$_2$](NO$_3$)$_2$



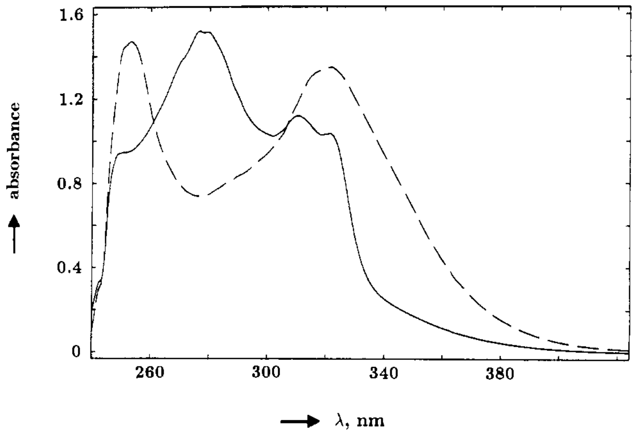


Figure 4. UV spectra of a 1:1 mixture of [Pd(bpy)$_2$](NO$_3$)$_2$ and [Pd(dtco)$_2$](NO$_3$)$_2$ in MeOH/H$_2$O (9:1) at 293 K before mixing (dashed line) and after mixing and standing (solid line).

In the thia complex [Pd(dtco)$_2$](NO$_3$)$_2$ as well as in the aza complexes [Ni(daco)$_2$](ClO$_4$)$_2$·2H$_2$O[5,6] and [Ni(daco)$_2$][B(C$_6$H$_5$)$_4$]$_2$(DMSO)$_2$,[22] the ligands have adopted a boat–chair conformation and the two C–H bonds pointing to the vacant axial sites of the metal (see Discussion above) are located on opposite sides of the coordination plane. So, from the structural point of view, the coordination of the dithia ligand dtco to the 4d^8 metal center Pd(II) corresponds very much to the coordination of the analogous diaza ligand daco to the 3d^8 center nickel(II).

Kinetics of Ligand Substitution. Substitution of the dtco ligands in the complex cation [Pd(dtco)$_2$]$^{2+}$ according to eqs 4 and 5 was

$$\mathrm{Pd(dtco)_2^{2+} + L\text{-}L \rightleftharpoons Pd(dtco)(L\text{-}L)^{2+} + dtco} \tag{4}$$

$$\mathrm{Pd(dtco)(L\text{-}L)^{2+} + L\text{-}L \rightleftharpoons Pd(L\text{-}L)_2^{2+} + dtco} \tag{5}$$

studied in a solvent mixture to provide for sufficient solubility of both of the organic ligands, L-L = bpy, phen, and the "salt" [Pd(dtco)$_2$](NO$_3$)$_2$. A 9:1 mixture of methanol and water turned out to be a very suitable medium in the sense that it allowed excess concentrations of the ligands L-L and guaranteed complete dissociation of the palladium complex as well (see conductivity data).

For the reaction with L-L = bpy and phen, the decrease in absorbance observed at 334 nm did not cover the full range expected for the formation of the complex [Pd(L-L)$_2$]$^{2+}$ according to eqs 4 and 5. Even at excess concentrations of L-L = bpy the final spectrum observed corresponds to the spectrum of the

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(22) Boeyens, J. C. A.; Fox, Ch. C. *S. Afr. J. Chem.* **1984**, *37*, 1.

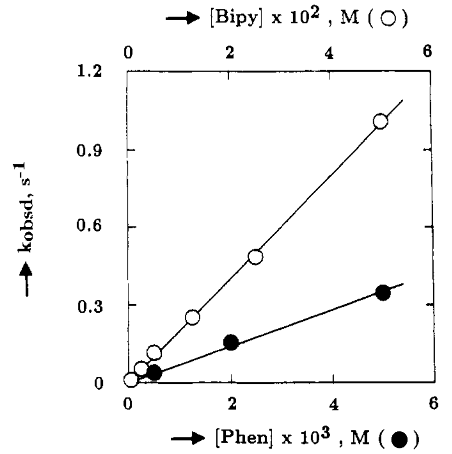

Figure 5. Plot of the experimental rate constant k_{obsd} for reaction 4 vs the concentration of the entering ligand L-L (bpy, phen) at 293 K in MeOH/H$_2$O (9:1) ([Pd(dtco)$_2$$^{2+}$] = 2.5 × 10^{-5} M).

mixed-ligand complex [Pd(dtco)(bpy)]$^{2+}$ instead (see Table II), which was also obtained when solutions of [Pd(dtco)$_2$]$^{2+}$ and [Pd(bpy)$_2$]$^{2+}$, as mixed in a molar ratio of 1:1, were equilibrated according to (6) (see Figure 4). . This means that the mixed

$$[\mathrm{Pd(dtco)_2}]^{2+} + [\mathrm{Pd(bpy)_2}]^{2+} \rightleftharpoons 2[\mathrm{Pd(dtco)(bpy)}]^{2+} \quad (6)$$

complex is thermodynamically more stable than the species [Pd(dtco)$_2$]$^{2+}$, [Pd(bpy)$_2$]$^{2+}$, and [Pd(phen)$_2$]$^{2+}$. An explanation for this lies probably in the steric hindrance arising from a planar arrangement of the two bpy or phen ligands in the corresponding bis complexes.[17] As a matter of fact, for both species [Pd(bpy)$_2$]$^{2+}$ and [Pd(phen)$_2$]$^{2+}$, a tetrahedral distortion by 24.0 and 18.7°, respectively, is found for the solid state.[23-25] One may conclude, therefore, that (i) bpy and phen are "stronger" ligands for Pd(II) than dtco and (ii) it is the planarity of the mixed-ligand species [Pd(dtco)(bpy)]$^{2+}$ and [Pd(dtco)(phen)]$^{2+}$ which makes them more stable than the corresponding distorted (bpy)$_2$ and distorted (phen)$_2$ complexes.

The mixed-ligand complexes [Pd(dtco)(bpy)]$^{2+}$ and [Pd(dtco)(phen)]$^{2+}$, formed in reaction 4, resemble in some way the mixed-ligand species [Ni(daco)(CN)$_2$]^0, as described by Billo[3], and [Ni(dto)(mnt)]$^{2-}$, as studied by Pearson and Sweigart[26] (dto^{2-} and mnt^{2-} are bidentate dithiolates). With an excess of entering ligand, however, these species are converted to [Ni(CN)$_4$]$^{2-}$ and [Ni(mnt)$_2$]$^{2-}$, respectively, which contrasts the behavior of the species [Pd(dtco)(L-L)]$^{2+}$ being stable in the presence of an excess of L-L.

The absorbance/time data for reaction (4) with L-L = bpy, phen could be fitted to eq 2, which means that ligand substitution according to (4) is first-order in [Pd(dtco)$_2$]$^{2+}$. Plotting of the pseudo-first-order rate constant k_{obsd} vs the excess concentration of L-L yields straight lines without intercept (see Figure 5), the slope of which corresponds to second-order rate constant k (see Table VI). So, ligand substitution according to (4) is governed by rate law (7).

$$-\mathrm{d}[\mathrm{Pd(dtco)_2}^{2+}]/\mathrm{d}t = k_{obsd}[\mathrm{Pd(dtco)_2}^{2+}] = k[\text{L-L}][\mathrm{Pd(dtco)_2}^{2+}] \quad (7)$$

A solvent-initiated pathway, as typically found for ligand substitution in square-planar Pt(II) and Pd(II) complexes,[27] is not observed.

The most convincing interpretation of rate law (7) is the operation of an associative (A) mechanism. The experimental finding that the stronger base phen is also the better nucleophile (k_{phen} = 3.5 k_{bpy}) is in line with an associative mode of activation. In addition, the negative entropy of activation found for the system [Pd(dtco)$_2$]$^{2+}$/bpy ($\Delta S^{\ddagger}$ = −32.2 ± 1.4 cal K^{-1} mol^{-1}, see Table VI) supports this interpretation.

Table VI. Second-Order Rate Constants (293 K) for Ligand Substitution in [Pd(dtco)$_2$]$^{2+}$ by Bidentate Ligands L-L in MeOH/H$_2$O (9:1) According to Reactions 4 and 5, respectively, at I = 0.1 M (NaNO$_3$)

L-L	L-L = bpy	L-L = phen	L-L = mnt^{2-}
Reaction 4: [Pd(dtco)$_2$]$^{2+}$ + L-L → [Pd(dtco)(L-L)]$^{2+}$ + dtco			
k^a, M^{-1} s^{-1}	20.0 ± 0.2^{a,b}	70.2 ± 2.1^{a,b}	>2 × 10$^{5\,c}$
$\Delta H^{\ddagger}$, kcal mol^{-1}	9.46 ± 0.44^d	not detm	
$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	−32.2 ± 1.4^d	not detm	
Reaction 5: [Pd(dtco)(L-L)]$^{2+}$ + L-L → [Pd(L-L)$_2$]$^{2+}$ + dtco			
k^a, M^{-1} s^{-1}	0	0	14.5 ± 0.2^{a,e}

[a] From the slope of the straight line obtained by plotting k_{obsd}[b] vs [L-L]$_0$ for different concentrations of L-L (see Figure 5); [Pd(dtco)$_2$$^{2+}$]$_0$ = 2.5 × 10^{-5} M. [b] Experimental rate constant k_{obsd} derived from the decrease in absorbance observed at 334 nm (see Table SV, supplementary material). [c] Estimated; the stopped-flow experiment produces a nontraceable jump in absorbance at 530 nm reflecting the fast reaction [Pd(dtco)$_2$]$^{2+}$ + mnt^{2-} → [Pd(dtco)(mnt)] + dtco. [d] From the temperature dependence of k as determined at five different temperatures in the range 293–318 K. [e] Experimental rate constant k_{obsd} derived from the decrease in absorbance observed at 530 nm for six different concentrations of mnt^{2-} in the range 5 × 10^{-4} to 2.5 × 10^{-2} M; [Pd(dtco)$_2$$^{2+}$]$_0$ = 5 × 10^{-5} M.

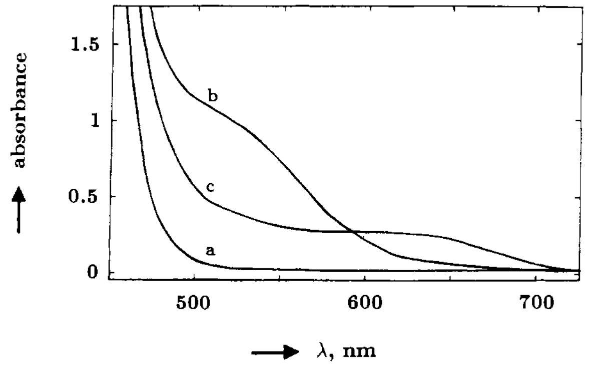

Figure 6. Vis spectra for the reaction of the cation [Pd(dtco)$_2$]$^{2+}$ with Na$_2$mnt (excess) in MeOH/H$_2$O (9:1) at 293 K: (a) spectrum before mixing; (b) spectrum immediately after mixing; (c) final spectrum after 2 min.

For the substitution of a monodentate ligand in square-planar complexes by another monodentate ligand according to (8), the

$$\mathrm{ML_3X} + \mathrm{Y} \rightleftharpoons \mathrm{ML_3Y} + \mathrm{X} \quad (8)$$

geometry of the transition state is assumed to be trigonal bipyramidal with X and Y occupying equatorial positions.[27] In principle, the incoming bidentate ligands bpy and phen could act as monodentates, although this is less conceivable for the rigid ligand phen. Taking the results of the X-ray structure analysis with "side-on coordination" of the nitrate ions as a meaningful indication for a special type of [Pd(dtco)$_2$]$^{2+}$/ligand interaction, one could also suggest a transition state for reaction 4 in which the entering ligands bpy and phen are coordinated as bidentates, thus formally producing coordination number 6 and a distorted "pseudo-octahedral" coordination for the palladium.

In contrast to ligand substitution with bpy and phen, with L-L = mnt^{2-}, both reactions 4 and 5 take place and can be observed. The stopped-flow experiment reveals a very fast initial step, which appears as a "jump in absorbance", turning the initially yellow-orange solution into a red solution with a strong absorption around 520 nm (shoulder; see Figure 6). This red solution then becomes green, which can be monitored by stopped-flow spectrophotometry. The kinetics of this red to green conversion again follow rate law (7) with L-L = mnt^{2-}, the resulting second-order rate constant

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(26) Pearson, R. G.; Sweigart, D. A. *Inorg. Chem.* **1970**, *9*, 1167.
(27) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, MA, 1974; Chapter IV.

$k = 14.5\ M^{-1}\ s^{-1}$ (see Table VI) being of the same order of magnitude as k_{bpy} and k_{phen}.

The sum of experimental findings for the system $[Pd(dtco)_2]^{2+}/mnt^{2-}$ leads to the interpretation that (i) the initial reaction of the anion mnt^{2-} with the cation $[Pd(dtco)_2]^{2+}$ to form the mixed-ligand species [Pd(dtco)(mnt)] is too fast for the stopped-flow time scale (one can estimate $k > 2 \times 10^5\ M^{-1}\ s^{-1}$), (ii) the red neutral intermediate [Pd(dtco)mnt)] with a strong absorption around 520 nm does not precipitate in the stopped-flow experiment because it is formed in low concentration ($[Pd(dtco)mnt] = [Pd(dtco)_2{}^{2+}]_0$) and, due to the excess condition $[mnt^{2-}]_0 \gg [Pd(dtco)_2{}^{2+}]_0$, is rapidly converted to the charged green product $[Pd(mnt)_2]^{2-}$ (see Figure 6), and (iii) the reaction of the neutral intermediate with the mnt^{2-} ioon is a second-order reaction following rate law (7) and, most probably, an associative mechanism.

The reaction of the cation $[Pd(dtco)_2]^{2+}$ with the dianion mnt^{2-} is by at least 4 orders of magnitude faster than its reaction with the neutral ligands bpy or phen. Taking into account initial outer-sphere complex formation, one can estimate on the basis of theoretical considerations[27] that the ratio $K_{os}(mnt^{2-})/K_{os}(bpy)$ should be on the order of 100, which would account for part of the rate effect observed. A substantial additional contribution comes probably from the different "nucleophilicity" of the entering ligands, as characterized by their $n_{Pt}°$ values.[27] It is well documented that sulfur-donor ligands such as thiocyanate, dimethyl sulfide or thiourea have much greater $n_{Pt}°$ values than corresponding nitrogen donor ligands, which means that the mnt^{2-} ion, as compared to bpy and phen, is also the "better", i.e., faster reacting nucleophile. In addition, one should keep in mind that the bidentate ligand mnt^{2-} is smaller than bpy and phen and its donor atoms are much more accessible so that coordination in a monodentate fashion is facilitated.

In conclusion, the present contribution provides detailed information on the structural properties of the novel dtco palladium(II) complexes $[Pd(dtco)Cl_2]$ and $[Pd(dtco)_2](NO_3)_2$ and presents data describing the kinetic properties of the species $[Pd(dtco)_2]^{2+}$ in ligand-substitution reactions. As far as the comparison $[M(dtco)_2]^{2+}$ vs $[M(daco)_2]^{2+}$ is concerned one learns that (i) the Cu^{2+} ion oxidizes the thia ligand dtco[20] so that the species $[Cu(dtco)_2]^{2+}$, corresponding to the aza species $[Cu(daco)_2]^{2+}$, is not obtained, (ii) the well-characterized and kinetically studied aza complex $[Ni(daco)_2](ClO_4)_2 \cdot 2H_2O$ has a thia analogue, $[Ni(dtco)_2](ClO_4)_2$,[9] which is thermodynamically not very stable and dissolves with loss of the dtco ligand, (iii) in both complexes $[Pd(dtco)Cl_2]$ and $[Pd(dtco)_2](NO_3)_2$ the cyclic thioether ligand dtco has a folded boat-chair conformation which is practically identical with the conformation of the ring skeleton found for the nickel(II) daco complexes $[Ni(daco)_2]X_2$ ($X = ClO_4$,[5,6] $B(C_6H_5)_4$[22]), (iv) ligand substitution in the cation $[Pd(dtco)_2]^{2+}$ by bidentate ligands obeys a simple second-order rate law and follows an associative mechanism, and (v) the reaction with even an excess of bpy and phen does not produce the bis complexes but, obviously for steric reasons, only the mixed-ligand species $[Pd(dtco)(bpy)]^{2+}$ and $[Pd(dtco)(phen)]^{2+}$, respectively.

The data presented do not allow a direct comparison of the relative reactivities of two species, $[M(dtco)_2]^{2+}$ and $[M(daco)_2]^{2+}$, in which the same metal cation coordinates either dtco or daco. Work on such a couple of complexes with M = Pd is in progress.

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Supplementary Material Available: Tables SI–SIII, listing complete crystallographic data, calculated coordinates of hydrogens, and thermal parameters, and Table SV, listing the complete set of experimental rate constants (5 pages); Table SIV, listing observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Ligation-Induced Changes in Metal–Metal Bonding in Luminescent Binuclear Complexes Containing Gold(I) and Iridium(I)

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Treatment of $[Ir(CO)ClAu(\mu\text{-dpm})_2](PF_6)$ (dpm is bis(diphenylphosphino)methane) with 2 or 3 equiv of methyl isocyanide and ammonium hexafluorophosphate yields $[Ir(CNCH_3)_2Au(\mu\text{-dpm})_2](PF_6)_2$ or yellow $[Ir(CNCH_3)_3Au(\mu\text{-dpm})_2](PF_6)_2$, respectively. Red crystals of $[Ir(CNMe)_2Au(\mu\text{-dpm})_2](PF_6)_2 \cdot CH_2Cl_2$ form in the monoclinic space group $P2_1/c$ (No. 14) with $a = 20.337$ (4) Å, $b = 12.633$ (2) Å, $c = 22.523$ (5) Å, and $\beta = 100.29$ (1)° at 130 K with $Z = 4$. Refinement of 4998 reflections and 450 parameters gave $R = 0.057$ and $R_w = 0.055$. The structure consists of a nearly planar $Ir(CNCH_3)_2P_2$ unit that is connected to a very linear AuP_2 unit through two dpm bridges. The Ir–Au distance is 2.944 (1) Å. The complex in dichloromethane solution shows a strong absorption at 492 nm ($\epsilon = 5100\ M^{-1}\ cm^{-1}$), which is assigned as the allowed $\sigma^*(d_{z^2}d_{z^2}) \rightarrow \sigma(p_zp_z)$ transition and photoemission at 540 nm (fluorescence) and 668 nm (phosphorescence). Yellow crystals of $[Ir(CNCH_3)_3Au(\mu\text{-dpm})_2](PF_6)_2$ form in the monoclinic space group $C2/c$ with $a = 30.511$ (8) Å, $b = 13.393$ (4) Å, $c = 28.859$ (8) Å, and $\beta = 99.10$ (2)° at 130 K with $Z = 8$. Refinement of 7605 reflections and 462 parameters gave $R = 0.0698$ and $R_w = 0.0534$. The structure is similar to that of $[Ir(CNCH_3)_2Au(\mu\text{-dpm})_2](PF_6)_2$ with an isocyanide added to the iridium along the Au–Ir axis. As a result, the Ir–Au distance has *shortened* to 2.817 (1) Å. The contraction is interpreted as resulting from the conversion into a species with an Ir → Au dative bond. The electronic absorption spectrum shows that the proximity-shifted band characteristic of $[Ir(CNMe)_2Au(\mu\text{-dpm})_2](PF_6)_2$ is no longer present. Rather shoulders at 332 ($\epsilon = 6700\ M^{-1}\ cm^{-1}$) and 298 ($\epsilon = 11000\ M^{-1}\ cm^{-1}$) are seen. In dichloromethane at 23 °C, there is a broad emission at 580 nm (with a lifetime of 1.2 μs), which shifts to 628 nm at −196 °C, that is assigned to an excited triplet state.

Introduction

Considerable attention has been given to the spectroscopic and bonding properties of dimeric complexes involving two face-to-face planar d^8 ions. Studies of the absorption spectra and of the long-lived excited states associated with complexes such as $Pt_2(P_2O_5H_2)_4{}^{4-}$,[1] $Ir_2(\mu\text{-pz})_2(COD)_2$ (pz is pyrazolyl, COD is 1,5-cyclooctadiene),[2] $Rh_2(CNR)_8{}^{2+}$,[3] and phosphine-bridged Rh(I)

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