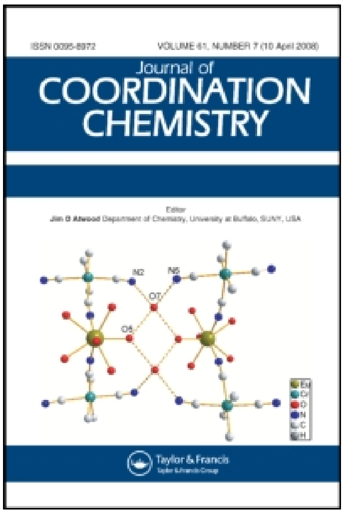

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PYRAZOLATO-BRIDGED BINUCLEAR COMPLEXES OF PLATINUM(II) WITH CARBONYL LIGANDS

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PYRAZOLATO-BRIDGED BINUCLEAR COMPLEXES OF PLATINUM(II) WITH CARBONYL LIGANDS

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The majority of complexes containing bridging pyrazolato ligands [pz = $C_3H_3N_2{}^{1-}$] have been shown to involve two or three bridging pz groups and to exhibit puckered MN_4M' central rings; however, several recent examples of homo and heterobinuclear complexes with single bridging ligands and essentially planar central rings have been reported. The synthesis and structural characterization of a new member of this series *trans*-[(CO)ClPt(μ-pz)(μ-Cl)PtCl(CO)] and its mononuclear precursor *trans*-[Pt(CO)(Cl)$_2$(Hpz)] are reported here.

The mononuclear complex *trans*-[PtCl$_2$(CO)(pzH)] crystallized in $P2_1$ with $a = 3.417(1)$, $b = 16.454(5)$, $c = 14.571(3)$ Å, $\beta = 90.60(2)°$, $V = 819.2(7)$ A^3, and $Z = 4$. The overall complex is planar and stacked with the plantinum centers aligned in the a direction. The intermolecular Pt-Pt distance of 3.417(0) Å indicates a weak bonding interaction (van der Waals contact = 3.6 Å).

The complex *trans*-(CO)ClPt(μ-Cl)(μ-pz)PtCl(CO) crystallized in $P2_1/c$ with $a = 6.781(6)$, $b = 17.750(4)$, $c = 9.869(7)$ Å, $\beta = 106.07(6)°$, $V = 1141(2)$ Å^3, and $Z = 4$. The complex is planar to within 0.1(8) Å. The molecules stack with nearly linear Pt-Pt chains (Pt-Pt-Pt angle = 166.8°). The shortest Pt-Pt intermolecular interactions are 3.399(5) and 3.427(5) Å.

KEYWORDS: platinum pyrazole, structure

INTRODUCTION

Pyrazole (pzH) is an excellent exobidentate bridging ligand[1] and has been used extensively for the production of binuclear and polynuclear complexes. The majority of known pyrazolide complexes involve two or three bridges between adjacent metal centers; however, several recent examples of bimetallic complexes with a single bridging pyrazolide group have been reported[2].

The binuclear complex *cis*-(μ-chloro)(μ-pyrazolide)dichloro-*bis*-(ethylene)diplatinum(II) [*1*] has been shown to exhibit a planar central structure[2(b)] with all atoms except those of the ethylene groups lying within 0.35(2)Å of the coordination plane

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of the two platinum atoms. The packing of the molecules in the unit cell suggested weak association of the molecules in pairs, presumably *via* London forces; however, the steric requirements of the out-of-plane C_2H_4 ligands limits the platinum-platinum contacts. The distances between the planes of adjacent complexes alternate between 3.77(1)Å and 3.96(1)Å. The closest approach between platinum atoms for this complex was 4.028(2) Å, significantly greater than the van der Waals contact distance of 3.6 Å[3]. As part of an investigation of the chemistry of this family of binuclear complexes, we have studied the displacement of the ethylene ligands of [*1*] with carbon monoxide. In part, we were interested in the degree to which intermolecular interaction could be enhanced by reduced axial interference. Replacement of the olefin ligands by carbon monoxide is a relatively common reaction[4]; however, the possibility for production of isomeric products leads to potential complication in this system. Characterization of the products of this reaction required a detailed study of the synthetic reaction by NMR spectroscopy and structural studies on isolated materials.

EXPERIMENTAL

Materials and Methods

All chemicals used were reagent grade or better and used without further purification unless otherwise noted. Deuterated solvents were used as supplied by Aldrich Chemical Company. Ethylene and carbon monoxide gases were C.P. grade (99.5%) from Air Products. Uncorrected melting point ranges were determined on a Thomas Hoover capillary melting point apparatus. The infrared spectra were recorded using a Perkin-Elmer 580B IR spectrophotometer and a Nicolet 20DX FTIR. Proton NMR spectra were obtained using Varian EM360 and Jeol FX90Q spectrometers. The carbon NMR spectra were obtained using the Jeol FX90Q spectrometers. Single crystal structural determinations were carried out using an Enraf-Nonius CAD4 diffractometer.

The complexes *cis*-(μ-chloro)(μ-pyrazolide)dichloro-*bis*-(ethylene)diplatinum(II) [*1*] and *trans*-dichloro(ethylene)(pyrazole)platinum(II) [*2*] were prepared as previously described by Deese[5].

trans-$Pt(Cl)_2(CO)(C_3H_4N_2)$ [*3*]

The complex *trans*-dichloro(carbonyl)(pyrazole)platinum(II) was prepared by dissolving 0.67 g (0.18 mmol) of *trans*-$Pt(Cl)_2(C_2H_4)(C_3H_4N_2)$ in 3.0–3.5 ml $CDCl_3$ and bubbling dry CO through the solution at ambient temperature for approximately 30 min. The proton NMR of the reaction was monitored for loss of the coordinated ethylene signal at δ = 4.73 ppm and shifts in the ring proton resonances for the pyrazole ligand. The reaction mixture was shaken with a small amount of animal charcoal, filtered, and reduced in volume by passing N_2 over the solution.

The yellow crystalline product formed upon evaporation of solvent (melting point range = 110–112°C). Samples from different preparations sent for elemental analysis consistently gave high %C and low %N; however, spectroscopic evidence and crystal determinations support the indicated stoichiometry.

[Cl(CO)Pt]₂$(\mu\text{-Cl})(\mu\text{-}C_3H_3N_2)$ [4]

The binuclear *bis*-carbonyl complex was prepared by displacement of ethylene from compound [*1*] by passing CO through a chloroform solution of the starting material. The solvent was purified by chromatography over alumina and the CO dried by passing the gas stream through a drying column containing $CaCl_2$ and Linde Type 4A molecular sieves. Preliminary studies indicated that the first displacement of ethylene is much faster than the second and that long reaction times lead to the precipitation of a brick-red solid that contains non-equivalent CO ligands and an exobidentate pyrazolide bridge. The most convenient synthetic method is to monitor the reaction by proton NMR and terminate the reaction before the red secondary product is formed. Precipitation of the yellow product [*4*] is most readily achieved by using a minimal amount of solvent in order to obtain a saturated solution and cooling the reaction mixture in an ice-water bath. Proton NMR confirms the absence of coordinated ethylene and the equivalence of H(2) and H(4) of the pyrazolide bridge required for a symmetrical binuclear product (melting point range = decomposition > 125°C). *Anal. calcd.* for $[Cl(CO)Pt]_2(\mu\text{-Cl})(\mu\text{-}C_3H_3N_2)$: C, 9.69; H, 0.49; N, 4.52. Found: C, 9.87; H, 0.57; N, 4.62.

Due to low solubility the red product obtained after long reaction times was only partially characterized. The carbon monoxide was passed through a solution of [*1*] until the proton and/or ^{13}C NMR spectrum indicated complete replacement of ethylene by CO (*ca.* 45 min). Further reaction with CO (*ca.* 1.5 h) led to the precipitation of a red finely divided solid which was filtered under N_2. When dry the material appears to be air stable. *Anal.* calcd. for $Pt_2(pz)Cl(CO)_2 \cdot 2CHCl_3$(%): C, 10.67; H, 0.63; N, 3.56. Found: C, 10.91; H, 0.73; N, 3.75.

RESULTS AND DISCUSSION

The synthesis of $[Cl(CO)Pt]_2(\mu\text{-Cl})(\mu\text{-}C_3H_3N_2)$ [*4*] by displacement of C_2H_4 from the corresponding *bis*-ethylene complex [*1*] proved to be more complicated than expected. Several products are produced, culminating with the formation of a chloroform insoluble red product [5] which contains both CO and bridging pyrazolide ligands (based on vibrational spectra). For this reason the synthesis of the mononuclear analog *trans*-$Pt(Cl)_2(CO)(C_3H_4N_2)$ was undertaken as a possible precursor to compound [*4*]. The displacement of C_2H_4 by CO can be followed by NMR and proceeds smoothly. Long reaction times were avoided as a secondary reaction of [*3*] with CO leads to unidentified dark green-black products with properties similar to those reported by Booth and Chatt[6] for the reaction of CO with $[PtCl_2(CO)_2]$ in wet benzene. NMR data for compound [*3*] are summarized in Table 1.

The results of the crystallographic structure determinations of [*3*] and [*4*] were affected by a paucity of data with $I > 3\sigma$ (I) and the dominance of the Pt contribution in the diffraction intensities. This was especially true for [*4*]. Thus the standard deviations of the positional parameters for the lighter atoms are relatively large, as are the sigmas for their derived bond distances and angles. Nevertheless the general features of interest to this study — the overall planarity of the complexes, the presence or absence of stacking, and the Pt...Pt distances — are revealed. The intensity symmetry of the reciprocal lattice of [*3*] is clearly monoclinic, but the beta

Table 1a 90 MHz Proton NMR Data.

	olefin δ(olefin)	$J(Pt^{195})$	δ(H-5)	$J(Pt^{195})$	azaromatic δ(H-3)	$J(Pt^{195})$	δ(H-4)	$J(Pt^{195})$
trans-$PtCl_2(pzH)(C_2H_4)$	4.73s	62.3 Hz	8.43m	15.7 Hz	7.74m		6.56m	–
trans-$PtCl_2(CO)(pzH)$			8.41m	14.4 Hz	7.78m	–	6.58m	–
trans-$(C_2H_4)ClPt(\mu\text{-}Cl)(\mu\text{-}pz)PtCl(C_2H_4)$	4.54s	56.1 Hz	8.16d	11.2 Hz	8.16d	11.2 Hz	6.27m	8.8 Hz
trans-$(CO)ClPt(\mu\text{-}Cl)(\mu\text{-}pz)PtCl(C_2H_4)$ [*in-situ*]	4.69s	56.4 Hz	–	–	–	–	–	–
trans-$(CO)ClPt(\mu\text{-}Cl)(\mu\text{-}pz)PtCl(CO)$	–	–	8.09d	–	8.09d		6.36m	7.6 Hz

[a] δ(N(2)H) - 12.2 [b] δ(N(2)H) = 12.0

Table 1b Proton decoupled 22.5 MHz Carbon-13 NMR Data.

	olefin δ(olefin)	$J(Pt^{195})$	δ(C-5)	$J(Pt^{195})$	azaromatic δ(C-3)	$J(Pt^{195})$	δ(C-4)	$J(Pt^{195})$
trans-$PtCl_2(C_2H_4)(pzH)$	72.2	180 Hz	139.5	48 Hz	130.3	30 Hz	106.8	34 Hz
trans-$PtCl_2(CO)(pzH)$[b]	–	–	136.9 Hz	46.9 Hz	131.3	28.1 Hz	107.4	29.7 Hz
trans-$(C_2H_4)ClPt(\mu\text{-}Cl)(\mu\text{-}pz)PtCl(C_2H_4)$	73.9	156.8 Hz	141.4	60.5 Hz[a]	141.4	37.1 Hz[a]	103.9	35.8 Hz
trans-$(CO)ClPt(\mu\text{-}Cl)(\mu\text{-}pz)PtCl(CO)$			141.2	57.3 Hz[a]	141.2	31.7 Hz[b]	104.9	31.7 Hz

[a] The C-5 and C-3 carbon atoms are chemically equivalent and are coupled to two non-equivalent Pt^{195} nuclei.
[b] δ(CO) = 151.4 hz

angle is near 90° and there is an approximate glide plane perpendicular to *a* along *c* and a non-space group translation of approximately (0.57, 0.0, 0.52) relating the two crystallographically independent molecules.

Crystals of [*3*] were grown by evaporation of a chloroform solution. The crystallographic data are summarized in Table 2. The general features of this complex are quite similar to those for the ethylene precursor [*2*][9] (also see Table 3). The coplanarity of the pyrazole ring plane and the coordination plane of the metal for both [*2*] and [*3*] (dihedral angles of 7.2° and 7.8°) appears to involve an intramolecular hydrogen bond between the ring NH and an adjacent Cl$^-$ ligand. The distances N(2) to Cl(2) and N(4) to Cl(4) are well inside the normal range for

Table 2 Summary of crystallographic data

formula	$C_4H_4Cl_2N_2OPt$	$C_5H_3Cl_3N_2O_2Pt_2$
fw	362.09	619.63
crystal size, mm	0.5 × 0.12 × 0.12	0.06 × 0.06 × 0.32
a, A	3.4175(14)	6.781(6)
b, A	16.454(5)	17.750(4)
c, A	14.571(3)	9.869(7)
β, deg	90.60(2)	106.07(6)
V, A^3	819.2(7)	1141(2)
no reflns cell detn	25	14
2θ, cell detn (deg)	16–20	15–19
d (calc), g cm^3	2.94	3.61
F (000)	648	1080
space group	$P2_1$	$P2_1/c$
crystal color	yellow needles	
Z	4	
radiation	MoK$_\alpha$	
λ, A	0.71073	
temp, K	293	
scan technique	$\theta/2\theta$	
scan width, deg	$1.0 + 0.35\tan\theta$	
diffractometer	Enraf-Nonius CAD4	
scan speed, deg min^{-1}	4–16	
absorption method	psi scans	analytical
2θ range, deg	2–25	2–18
h, k, l ranges	0,4; −19,19; −17,17	0,7;0,20; −11,11
linear abs coeff, cm^{-1}	179	254
exposure time, hrs	32	14.4
decay correction, ±%	0.97–1.01	0.95–1.06
absorption correction	0.55–1.00	0.77–1.00
unique refl	1724	1795
data with $F^2 > 3\sigma(F^2)$	817	530
parameters refined	111	83
R (F^2)	0.045	0.100
Rw (F^2)	0.055	0.116
GOF	1.0	1.9
p in $w = [\sigma(I) + pI^2]/4F$	0.08	0.08
final diff map, e A^{-3}	−1.7(3) to +2.4(3)	−2.9(7) to +4.3(7)
largest Δ/σ	0.2	0.1
extinction correction	5.8E-08	
H atom treatment	fixed(C − H = 0.95 A, B = 1.2*B of carbon)	
programs	Enraf-Nonius SDP	
scattering factors	Internat. Tables Crystallography Vol. 4	

Table 3 Selected interatomic distances (Å) and angles (deg) with esd's in parentheses for *trans*-$PtCl_2(C_3H_4N_2)(CO)$.

atoms	distance (Å)	atoms	distance (Å)
Pt(1)-Cl(1)	2.294(14)	Pt(2)-Cl(3)	2.29(2)
Pt(1)-Cl(2)	2.279(15)	Pt(2)-Cl(4)	2.29(2)
Pt(1)-C(1)	1.78(6)	Pt(2)-C(5)	1.77(8)
Pt(1)-N(1)	2.06(4)	Pt(2)-N(3)	2.11(5)
C(1)-O(1)	1.10(7)	C(5)-O(2)	1.02(8)
N(1)-N(2)	1.25(5)	N(3)-N(4)	1.15(8)
N(1)-C(2)	1.33(6)	B(3)-C(6)	1.38(7)
N(2)-C(4)	1.61(7)	N(4)-C(8)	1.39(9)
C(2)-C(3)	1.32(7)	C(6)-C(7)	1.34(8)
C(3)-C(4)	1.24(7)	C(7)-C(8)	1.22(8)
N(2)-Cl(2)	2.81(5)	N(4)-Cl(4)	3.02(7)
atoms	angle (deg)	atoms	angle (deg)
Cl(1)-Pt(1)-C(2)	178.8(5)	Cl(3)-Pt(2)-Cl(4)	177.0(9)
Cl(1)-Pt(1)-C(1)	91.0(19)	Cl(3)-Pt(2)-C(5)	94.2(28)
Cl(1)-Pt(1)-N(1)	90.8(11)	Cl(3)-Pt(2)-N(3)	92.2(13)
Cl(2)-Pt(1)-C(1)	89.4(19)	Cl(4)-Pt(2)-C(5)	88.8(28)
Cl(2)-Pt(1)-N(1)	88.8(11)	Cl(4)-Pt(2)-N(3)	84.9(14)
C(1)-Pt(1)-N(1)	175.8(17)	C(5)-Pt(2)-N(3)	173.5(28)
Pt(1)-C(1)-O(1)	172(5)	Pt(2)-C(5)-O(2)	155(9)
Pt(1)-N(1)-N(2)	115(3)	Pt(2)-N(3)-N(4)	131(5)
Pt(1)-N(1)-C(2)	132(3)	Pt(2)-N(3)-C(6)	127(4)
N(1)-C(2)-C(3)	111(5)	N(3)-C(6)-C(7)	111(6)
N(2)-N(1)-C(2)	113(4)	N(4)-N(3)-C(6)	101(6)
C(2)-C(3)-C(4)	110(5)	C(6)-C(7)-C(8)	105(7)
C(3)-C(4)-N(2)	106(5)	C(7)-C(8)-N(4)	106(6)
C(4)-N(2)-N(1)	101(4)	C(8)-N(4)-N(3)	116(6)

NH··· Cl hydrogen bonds.[7,8] This is supported by the appearance of a sharp band in the infrared spectrum at 3300 cm^{-1}.

The molecules are stacked along the short *a* axis of the crystal with the platinum atoms aligned with separation slightly less than the van der Waals contact distance. The intermolecular distances are shorter in the carbon monoxide complex (3.417(0)Å) than for the corresponding ethylene species indicating that the axial steric hindrance of the olefin ligands must play a significant role in determining the crystal packing for *trans*-$Pt(Cl)_2(C_2H_4)(pzH)$. The intra- and inter-molecular distances and angles for compound [*3*] are given in Table 3. An ORTEP diagram showing the stacking in the solid is given in Figure 1. The ν(CO) for complex [*3*] is 2110 cm^{-1}, slightly lower than usual for platinum(II) carbonyls,[4] but normal for a metal carbonyl with moderate d_π-p_π backbonding. Based upon the properties of [*3*], the reaction of [*1*] with CO was re-examined with the assumption that the insoluble red product obtained for long reaction times was the result of a secondary reaction of compound [*4*].

Extensive ^1H and ^{13}C NMR studies of reactions of [*1*] with CO were undertaken. Due to the sensitivity of Pt(II) carbonyls to moisture, tank gases were passed through a drying tube layered with $CaCl_2$ and Type 4A molecular sieves. The solvents $CHCl_3$ and $CDCl_3$ were dried over alumina immediately prior to use. In preliminary experiments, CO was bubbled through the reaction mixture and aliquots withdrawn periodically for NMR analysis. Prior to obtaining spectra, the

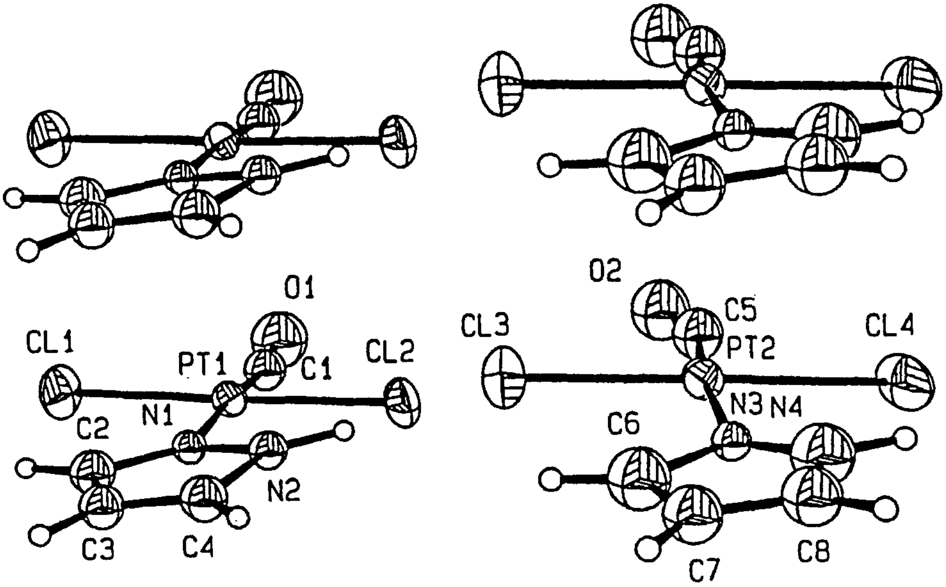

Figure 1 *An ORTEP drawing of [3] (30% ellipsoids) showing the atom numbering scheme and the* stacking of the two independent molecules.

samples were purged with N_2 to remove excess CO. This served to slow further reaction and reduce line broadening due to exchange of coordinated and free CO (or CO/C_2H_4 mixture). While not isolated, the monosubstituted product $(Cl)(CO)Pt(\mu\text{-}Cl)(\mu\text{-}C_3H_3N_2)Pt(C_2H_4)(Cl)$ can be inferred from the initial replacement of the peak at $\delta = 4.54$ in the ^1H spectrum of a reaction mixture by a signal at $\delta = 4.69$ with appropriate ^{195}Pt coupling. As the displacement of ethylene continues, this intermediate disappears yielding a solution in which only ring proton resonances are observed. The displacement of ethylene by CO can be reversed by subsequent reaction with C_2H_4. The NMR parameters for these products are summarized in Table 1.

Crystals of [*4*] were grown directly from a reaction mixture at reduced temperature. The crystallographic data for this compound are summarized in Table 2. The binuclear complex [*4*] is planar to within 0.1(8) Å. The main deviation from planarity occurs in the Pt-CO linkages. Bond distances and angles for the molecule summarized in Table 4 are comparable to those for similar structures.[2,9] An ORTEP diagram illustrating the crystal packing is shown in Figure 2. As in the case of [*3*], comparison of the intermolecular distances in [*4*] to those for compound [*1*] show the reduction of axial steric repulsion which allows for much shorter Pt-Pt contacts at an average of 3.413(5) Å as opposed to 4.028(2) Å for the olefin complex [*1*]. The distances between molecular planes are shorter and more nearly equal (3.373(5) and 3.401(5) Å) for [*4*] than for [*1*].

Compound [*4*] in $CHCl_3$ reacts further with CO to yield a brick-red insoluble product [*5*]. The diffuse reflectance FTIR spectrum of this material indicates the presence of terminal carbonyl ligands ($\nu(CO) = 2137$, 2097, and 2068 cm^{-1}). The presence of a bridging pyrazolato group is suggested by bands at 3158, 3128, and

Table 4 Selected interatomic distances (Å) and angles (deg) with esd's in parentheses for [(CO)ClPt]$_2$(μ-Cl)(μ-C$_3$H$_3$N$_2$); [*4*]

atoms	distance (Å)	atoms	angle (deg)
Pt(1)-Pt(2)	3.720(4)	Pt(1)-Cl(2)-Pt(2)	106.2(7)
Pt(1)-Cl(1)	2.280(25)	Cl(2)-Pt(1)-N(1)	92.7(16)
Pt(2)-Cl(3)	2.287(22)	Cl(2)-Pt(2)-N(2)	86.7(15)
Pt(1)-Cl(2)	2.312(20)	Cl(1)-Pt(1)-N(1)	90.3(17)
Pt(2)-Cl(2)	2.339(19)	Cl(3)-Pt(2)-N(2)	95.3(17)
Pt(1)-N(1)	2.01(4)	Pt(1)-N(1)-N(2)	117(4)
Pt(2)-N(2)	1.97(6)	Pt(2)-N(2)-N(1)	136(4)
Pt(1)-C(2)	1.98(8)	Cl(1)-Pt(1)-C(2)	91(3)
Pt(2)-C(1)	1.87(6)	Cl(3)-Pt(2)-C(1)	86(2)
C(1)-O(1)	1.05(6)	Pt(2)-C(1)-O(1)	176(7)
C(2)-O(2)	1.16(7)	Pt(1)-C(2)-O(2)	175(9)
N(1)-N(2)	1.34(7)	Cl(1)-Pt(1)-Cl(2)	177.0(6)
N(1)-C(5)	1.30(10)	Cl(2)-Pt(2)-Cl(3)	176.6(10)
N(2)-C(3)	1.48(10)	N(1)-N(2)-C(3)	95(6)
C(3)-C(4)	1.16(10)	N(2)-C(3)-C(4)	130(9)
C(4)-C(5)	1.40(11)	C(3)-C(4)-C(5)	87(8)
		C(4)-C(5)-N(1)	125(8)

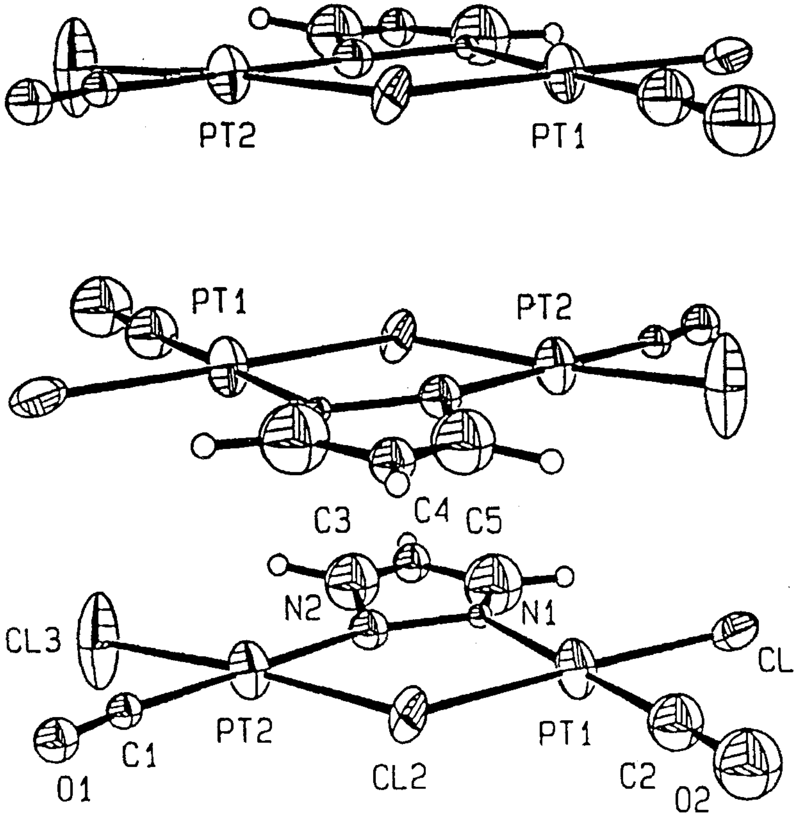

Figure 2 An ORTEP drawing of [*4*] (30% ellipsoids) showing the atom numbering scheme and the head-to-tail stacking along the *a* direction of the crystal.

3106 cm^{-1} (aromatic CH stretch), the absence of a ν(NH) in the 3300 cm^{-1} region, and presence of bands near 1300 and 615 cm^{-1} (characteristic of bridging pyrazolide). The 90 MHz proton NMR spectrum of the filtrate shows only the presence of compound [*4*] and a small amount of [*3*]. Attempts to grow crystals of this material have been unsuccessful to date. Further work in the characterization of this material is in progress.

CONCLUSIONS

The complexes [*1*] and [*4*] are part of a small but growing family of binuclear complexes of d^8 metal ions with singly bridging pyrazolato ligands. With the exception of $[Rh(CO)_2]_2(\mu\text{-}Cl)(\mu\text{-}C_3H_3N_2)$,[2(d)] these materials are essentially planar rather than the 'boat' conformer characteristic of complexes of these metals containing two μ-pyrazolato ligands. The planarity of the central core of the binuclear complexes suggests potential for stacking of these complexes to form materials with metal-metal bonded chains. The short Pt-Pt distances indicate a weak bonding interaction in the solid state and suggests that partial oxidation could lead to materials with stronger metal-metal bonding.

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