moiety show no significant differences with those found in comparable complexes (Schrauzer *et al.*, 1983, and references therein). The most noticeable feature of this structure is an unsymmetrical mode of interaction between the oxo groups and the Si atoms. O1 is in close contact with Si1 and Si2 with shorter distances than the corresponding van der Waals interaction (3·6 Å): O1 is 3·32 (1) Å distant from Si1 and Si2 whereas O2 is at 3·95 (1) Å from Si1 and Si2. More pronounced are the differences in the torsional angles. Thus O1—Mo—C11—Si1 and O1—Mo—C15—Si2 angles are −27 and +25° and O2—Mo—C11—Si1 and O2—Mo—Si2—C15 angles are +86 and −88° respectively. Crystal packing cannot account for these intramolecular interactions, the molecules of the title compound being packed without any remarkable close contact.

Although it is premature to draw definite conclusions, it is likely that both structural features and electronic effects due to silicon (Ibrahim & Jorgensen, 1989) could account for the stability of the cationic species obtained by a hydrogen abstraction from $Mo(O)_2(bpy)(CH_2SiMe_3)_2$.

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(4,4'-Dimethyl-2,2'-bipyridyl-N,N')bis(isocyanato)platinum(II)

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Abstract. $[Pt(NCO)_2(C_{12}H_{12}N_2)]$, $M_r = 463·37$, orthorhombic, $Cmc2_1$, $a = 18·722$ (6), $b = 11·889$ (5), $c = 6·688$ (5) Å, $V = 1488·7$ (9) Å^3, $Z = 4$, $D_x = 2·067$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 90·59$ cm^{-1}, $F(000) = 864$, $T = 291$ (1) K, $R = 0·052$ for 735 reflections with $F \geq 6\sigma_F$. The structure consists of square-planar coordinated Pt atoms, surrounded by four N atoms; of these, two belong to the bidentate bipyridyl ligand and two belong to the two pseudohalide groups which occupy *cis* positions. The bite angle of the bipyridyl ligand is 82·3 (9)°, significantly larger than the value reported earlier for the unsubstituted bipyridyl ligand, 76 (2)°. The metal atom is displaced 0·10 (5) Å below the plane of the four N atoms. The non-bonding Pt–Pt distance is 0·258 (5) Å longer in the title compound than in the unsubstituted ligand complex, leading to significant differences in the chemical and spectroscopic properties of the two homologues.

Introduction. Complexes of Pt^{II} generally exhibit square-planar coordination around the metal atom with sp^2d hybridization of the metal orbitals. In a number of such complexes, an interesting color change can be observed on heating the neat compounds (Rosenblatt & Schleede, 1933; Schilt, 1962, 1963; Textor & Oswald, 1974; Che, He, Poon & Mak 1989). These changes have been associated with a change in the bonding mode of a polydentate ligand, with hydration changes (Bielli, Gidney, Gillard & Heaton, 1974) and/or with stacking of the monomer units to optimize orbital overlap of the d_z2p_z orbitals and concomitant interaction between adjacent Pt atoms. In an effort to understand the detailed

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molecular-level architecture of such complexes, in which two polyatomic (pseudohalide) ligands are unambiguously *cis* to each other, the crystal structure of Pt(bpy)(NCO)$_2$ (bpy = 2,2'-bipyridyl) [Pt(NCO)$_2$(C$_{10}$H$_8$N$_2$)] (1) was recently reported (Coyer, Herber & Cohen, 1990). In the present study the structure of the related complex Pt(dmbpy)-(NCO)$_2$ (dmbpy = 4,4'-dimethyl-2,2'-bipyridyl) [Pt(C$_{12}$H$_{12}$N$_2$)(NCO)$_2$] (2) has been elucidated.

Experimental. Pt(dmbpy)(NCO)$_2$ was prepared by converting K$_2$PtCl$_4$ to Pt(dmbpy)Cl$_2$, treating this with twice the stoichiometric amount of aqueous AgClO$_4$ in Me$_2$SO solution to afford the bis-aqua complex, and converting this to the title compound by treatment with KNCO at 273 K. The crude bright orange product was recrystallized from *N*-methyl pyrrolidone to give bright orange needle shaped crystals which were used for data collection. IR of the solid: ν_{CN} at 2290 (*s*, sh), ν_{CO} at 1350, 1337 cm^{-1} (*s*). ^{13}C NMR in *N*-methyl pyrrolidone: N^{13}CO at 124·86 p.p.m.

A crystal 0·1 × 0·2 × 0·4 mm was used for data collection on a PW1100/20 Philips four-circle computer-controlled diffractometer. Mo *K*α (λ = 0·71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. Unit-cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range 10 ≤ θ ≤ 13°. Intensity data were collected using the ω–2θ technique to a max. 2θ of 55°. Scan width, Δω, for each reflection was (1·00 + 0·35tanθ)° with a scan speed of 3·0° min^{-1}. Background measurements were made for 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in the intensities were found. Indices *hkl*: 0 ≤ *h* ≤ 23; 0 ≤ *k* ≤ 15; 0 ≤ *l* ≤ 8. 1011 reflections measured, 942 unique reflections, and 735 reflections with $F \geq 6\sigma_F$.

Intensities were corrected for Lorentz, polarization and absorption effects (max. and min. transmission values 0·2126 and 0·1925). Refinement was anisotropic for the Pt atom only. All non-H atoms were found using the results of the *SHELXS*86 (Sheldrick, 1985) direct-method analysis. After several refinements the positions of the H atoms were calculated and added, with a constant isotropic temperature factor of 0·08 Å^2, to the refinement process. Refinement proceeded to convergence by minimizing the function $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma_F^2 + 0·006217F^2$, $R = 0·052$, $wR = 0·083$, $S = 1·83$. 49 parameters were refined, max. $\Delta/\sigma = 0·018$. A final difference Fourier synthesis map showed several peaks less than 2 e Å^{-3} scattered about the unit cell without a significant feature. Atomic scattering factors and calculations from *SHELX*76 (Sheldrick, 1976).

All computing carried out on a CYBER 855 computer at the Hebrew University of Jerusalem.

Discussion. The positional parameters for (2) are summarized in Table 1* and the atom-numbering scheme is shown in Fig. 1. Selected bond lengths and bond angles are summarized in Table 2. The structure consists of a nearly square planar array of four N atoms (two belonging to the bipyridyl ligand and two belonging to the cyanato groups) around the metal atom, and is very similar to the structure of the unsubstituted complex (1) reported earlier (Coyer, Herber & Cohen, 1990). There are, however, a number of significant differences. The Pt—N(1) and Pt—N(2) distances in (1) and (2) are essentially the same, but the bite angle [N(1)—Pt—N(1)'] of the bidentate ligand is larger in (2) [82·3 (6)°] than in (1) [76 (2)°] with a concomitant decrease in the N(2)—Pt—N(2') bond angle from 94 (2) to 90 (1)°. The two six-membered rings are planar with an average deviation from the least-squares plane of 0·0149 Å. As in all other crystallographically studied transition metal cyanates with monodentate binding the pseudohalide ligand, the cyanate group in this complex, is bonded through the N atom. Attempted refinement of the structure with the cyanate group O-bonded gave larger *R* and *wR* values, as well as unreasonable bond-distance ratios.

Of particular interest with respect to molecular stacking in the solid is the observation that the Pt—Pt distance is 3·235 (5) in (1) and 3·4934 (7) Å in (2), presumably owing to the steric requirements of the two methyl groups in the latter. The Pt atom is located 0·10 (5) Å below the plane of the four nearest neighbor N atoms, significantly affecting the metal atom hybridization. The molecular stacking in the unit cell is, as expected from minimization of Coulombic repulsion effects, with adjacent molecules having their bipyridyl ligands oriented in opposite directions with respect to the normal to the molecular symmetry axis. This axis arises because the two parts of the molecule are related to each other by a *mirror plane*, operation $-x$, y, z, crossing the Pt atom. A similar stacking arrangement has been reported for Pt(en)Cl$_2$ (en = ethylenediamine) (Textor & Oswald, 1974; Martin, Jacobson, Winter & Benson, 1970). Because of the differences in the two halves of the molecule, this stacking results in a non-superposition of the metal atoms (parallel to the c direction) which form a zigzag chain, with a Pt–Pt distance which is significantly longer than has been

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

	x	y	z	$B_{eq}(\text{Å}^2)$
Pt	0·0	0·54255 (9)	0·35	2·76 (4)
N(1)	0·0713 (8)	0·414 (1)	0·360 (7)	2·4 (2)
C(1)	0·140 (1)	0·424 (2)	0·375 (7)	3·6 (5)
C(2)	0·185 (1)	0·329 (2)	0·384 (5)	3·9 (5)
C(3)	0·156 (1)	0·222 (2)	0·365 (9)	4·0 (5)
C(4)	0·080 (1)	0·212 (2)	0·357 (9)	3·4 (3)
C(5)	0·039 (1)	0·310 (2)	0·350 (8)	3·1 (3)
C(6)	0·202 (1)	0·117 (2)	0·387 (6)	4·3 (6)
N(2)	0·074 (1)	0·658 (2)	0·37 (1)	5·3 (6)
C(7)	0·100 (1)	0·751 (2)	0·377 (4)	2·7 (5)
O	0·131 (1)	0·842 (2)	0·381 (7)	6·9 (6)

Table 2. *Selected bond lengths (Å) and angles (°)*

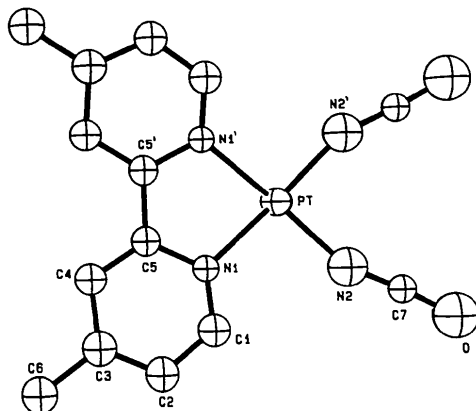| Pt—N(1)	2·03 (1)	C(3)—C(4)	1·43 (3)
Pt—N(2)	1·96 (2)	C(3)—C(6)	1·53 (4)
N(1)—C(1)	1·29 (3)	C(4)—C(5)	1·39 (3)
N(1)—C(5)	1·39 (3)	C(5)—C(5')	1·47 (3)
N(1)—C(2)	1·41 (3)	N(2)—C(7)	1·21 (3)
C(2)—C(3)	1·38 (3)	C(7)—O	1·22 (3)
N(1)—Pt—N(2)	93·4 (8)	C(2)—C(3)—C(4)	118 (2)
N(1)—Pt—N(1')	82·3 (6)	C(2)—C(3)—C(6)	122 (2)
N(1)—Pt—N(2')	173 (2)	C(4)—C(3)—C(6)	119 (2)
N(2)—Pt—N(2')	90 (1)	C(3)—C(4)—C(5)	118 (2)
Pt—N(1)—C(1)	126 (1)	N(1)—C(5)—C(4)	121 (2)
Pt—N(1)—C(5)	113 (1)	N(1)—C(5)—C(5')	116 (2)
C(1)—N(1)—C(5)	121 (2)	C(4)—C(5)—C(5')	123 (2)
N(1)—C(1)—C(2)	122 (2)	Pt—N(2)—C(7)	159 (2)
C(1)—C(2)—C(3)	120 (2)	N(2)—C(7)—O	176 (2)

Fig. 1. View of the title compound showing the atom-numbering scheme. The two pseudohalide ligands and the bpy rings are related by a mirror plane.

reported for (1). This distance is comparable to that reported in a number of non-conducting platinum pseudohalide complexes in which the metal atom is exclusively in the divalent state (Williams, 1983).

The infrared, ^{1}H and ^{13}C NMR, and UV-VIS spectroscopies of the title compound are not otherwise remarkable, and will be published elsewhere (Coyer & Herber, 1991).

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Crystal Structures of Bis(di-2-pyridylamine)(acetato)copper(II) Nitrate and Bis(di-2-pyridylamine)(formato)copper(II) Tetrafluoroborate

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Abstract. Bis(di-2-bipyridylamine)(acetato)copper(II) nitrate, $[Cu(C_{10}H_9N_3)_2(C_2H_3O_2)][NO_3]$, (I), $M_r =$ 526·89, and bis(di-2-bipyridylamine)(formato)copper(II) tetrafluoroborate, $[Cu(C_{10}H_9N_3)_2(CHO_2)][BF_4]$, (II), $M_r = 537\cdot64$, both crystallize in the monoclinic space group $P2_1/c$. (I), $a = 13\cdot216$ (3),

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