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Complexes of Tetracyanobiimidazole. 3. Platinum and Palladium Species

P. G. RASMUSSEN*, O. H. BAILEY

Department of Chemistry, University of Michigan, Ann Arbor, Mich. 48109, U.S.A.

and J. C. BAYÓN*

Department de Química Inorgànica, Facultat de Ciències, Universitat Autònoma de Barcelona, Bellaterra, Barcelona, Spain

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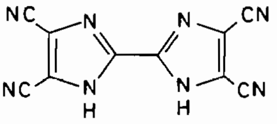
In this paper we describe monomeric complexes of Pd(II) and Pt(II) with 4,4′,5,5′-tetracyano-2,2′-biimidazole (H_2*Tcbiim). These compounds always contain the dianion (Tcbiim*$^=$*) in accord with the greater acidity expected for the cyanosubstituted ring system. The structure of* $[N(Bu)_4]_2[Pt(CN)_2Tcbiim)]$ *was determined by x-ray crystallography. The composition* $PtC_{44}H_{72}N_{12}$ *crystallizes in the* $P\bar{1}$ *triclinic space group with* $a = 16.664(3)$ Å, $b = 12.422(4)$ Å, $c = 13.842(4)$ Å, $\alpha = 112.47(2)$, $\beta = 111.01(2)$, $\gamma = 89.40(2)$ *and Z = 2 molecules/cell. A final agreement of* $R = 0.038$ *was obtained for 5359 observed reflections. The structure confirms planar bidentate chelation by Tcbiim*$^=$ *and an irregular square planar coordination for the platinum atom. The preparation of a series of salts* $M[Pt(CN)_2(Tcbiim)]$, $M = NBu_4^+$, NH_4^+, Ba^{2+}, *and for* K^+ *both the platinum and palladium analogs, are described. The neutral molecule Pt(COD)Tcbiim was also prepared. Activity of these species under oxidation conditions are discussed in relation to the pi accepting properties of the title ligand.*

Introduction

We have previously reported [1] the synthesis and some of the properties of a novel new compound 4,4′,5,5′-tetracyano-2,2′-biimidazole (H_2Tcbiim), *1*. We have also reported its use in forming complexes with Rh(I), Ir(I) and Mo(0) [2–4]. In this communication we report on compounds formed with divalent platinum and palladium.

These compounds were prepared as part of an effort to study deliberately synthesized analogues to partially oxidized, anisotropically conducting materials such as the Krogmann salts [5]. This field was reviewed recently by Williams [6], and it is evident that the range of examples is relatively narrow. We were particularly interested in exploring the use of the planar tetracyanobiimidazole dianion as a substitute for two cyanide ligands since its pi accepting properties should be similar. We were also interested in elaborating the use of tetracyanobiimidazole a pi accepting anionic ligand in concert with other ligands of low donor strength for synthetic purposed in organoplatinum chemistry.



Experimental

The compounds *cis*-$Pt(CN)_2(NH_3)_2$, $Pt(COD)Cl_2$, and H_2Tcbiim were prepared following published procedures [1, 7, 8]. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan. Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 1330 spectrophotometer. Fourier transform NMR were obtained on a Bruker WM-360 spectrometer calibrated with ^{13}C and ^{31}P shifts as positive downfield relative to TMS and H_3PO_4.

Preparation of $K_2[Pd(CN)_2Tcbiim]$ 2

500 mg of $K_2[Pd(CN)_4]3H_2O$ (1.46 mmol) and 335 mg of H_2Tcbiim (1.43 mmol) were refluxed in 25 ml of water. After 20 minutes the solution turned clear. Further refluxing for 3 hours, followed by cooling on ice produced a white precipitate. The ppt was filtered and washed with 3 ml of cold water and 10 ml of acetone. Yield 600 mg (90%). *Anal.* Calcd for $PdK_2C_{12}N_{10}$: C, 30.74; N, 29.88. Found: C, 30.66; N, 29.77%.

Preparation of $(NH_4)_2[Pt(CN)_2Tcbiim]$ 3

The method described for the palladium complex above gives yields of less than 5% for the platinum

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*Authors to whom all correspondence should be addressed.

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complex. Addition of varying quantities of HCl did not improve the yields. Instead, 600 mg of *cis*-$Pt(NH_3)_2(CN)_2$ (2.13 mmol) were added in small portions to a solution of 500 mg of H_2Tcbiim (2.13 mmol) in 200 ml of boiling water over a period of 15 minutes with strong stirring. The volume was reduced to 30 ml, filtered to remove traces of $Pt(CN)_2$ and furthered reduced to 10 ml. Addition of 15 ml methanol–150 ml ether resulted in precipitation. Yield 970 mg (90%). *Anal.* Calcd for $PtC_{12}N_{12}H_8$: C, 27.97; N, 32.62; H, 1.56. Found: C, 27.78; N, 32.47; H, 1.70%. ^{13}C NMR (D_2O): 153.1, 124.2, 121.3, 116.4, 114.2, 108.4.

Preparation of $(NBu_4)_2[Pt(CN)_2Tcbiim]$ 4

To a solution of *3* in water, the stoichiometric amount of NBu_4Br was added producing a white precipitate. It was recrystallized from acetone–methanol. *Anal.* Calcd for $PtC_{44}N_{12}H_{72}$: C, 54.80; N, 17.43; H, 7.52. Found: C, 54.72; N, 17.24; H, 7.47%.

Preparation of Pt(COD)Tcbiim 5

100 mg of $Pt(COD)Cl_2$ (0.27 mmol) and 63 mg of H_2Tcbiim (0.27 mmol) were refluxed in 80 ml of ethanol for 45 minutes. Upon cooling a precipitate formed which was filtered and washed with acetone and methylene chloride. Yield 122 mg (90%). *Anal.* Calcd for $PtC_{18}N_8H_{12}$: C, 40.38; N, 20.93; H, 2.26. Found: C, 40.16; N, 20.71; H, 2.35%.

TABLE I. Infrared Absorptions (cm^{-1}).

	Nitrile	Cyanide
$K_2[Pd(CN)_2Tcbiim]$	2244	2164, 2150
$K_2[Pt(CN)_2Tcbiim]$	2240	2162, 2143
$(NH_4)_2[Pt(CN)_2Tcbiim]$	2240	2160, 2137
$(NBu_4)_2[Pt(CN)_2Tcbiim]$	2230	2149, 2137
Pt(COD)Tcbiim	2240, 2229	

Collection and Solution of the X-ray Data

Well formed crystals of *4* were grown by slow evaporation of an acetone-methanol solution. A parallelepiped shaped crystal of dimensions 0.103 × 0.246 × 0.407 mm was mounted on a Syntex $P\bar{1}$ four circle diffractometer. Centering on 15 reflections yielded cell parameters of the triclinic system. The structure refined successfully in the space group $P\bar{1}$. A summary of crystal data is presented in Table II and programs are cited in footnote [9]. The structure was solved by conventional heavy atom and difference Fourier methods. After refining to isotropic convergence the data was corrected for absorption. Hydrogen atom positions were calculated and added to the refinement (R = 0.065, R_w = 0.079). Anisotropic refinement of the non-hydrogen atoms led to final values of R = 0.038, R_w = 0.048. The final difference map showed the highest peak in the vicinity of a heavy atom with intensity 1.59 e/Å^3.

TABLE II. Crystal Parameters for $(NBu_4)_2[Pt(CN)_2Tcbiim]$.

Space group	$P\bar{1}$
a, Å	16.664(3)
b, Å	12.422(4)
c, Å	13.842(4)
α, deg.	112.47(2)
β, deg.	111.01(2)
γ, deg.	89.40(2)
Mol. Wt.	964.22
Z	2
Calcd. density	1.17
Crystal Dimensions mm	(010)–0.103 $(10\bar{1})$–0.246 (100)–0.407
Radiation Å	λ(Mo K_α) 0.71069 Monochromatized from graphite crystal
Linear Absorption coefficient μ,	29.28 cm^{-1}
Scan speed, deg./min.	variable 2.5–12
Ratio background/peak scan	0.8
Std. reflections	$(6\bar{3}2)$ $(82\bar{4})$ $(4\bar{2}0)$
Scan range 2θ, deg.	0–45
Reflections collected	6842
Reflections observed $F^2 \geq 3\sigma(F^2)$	5359

Discussion

An ORTEP view of the structure of the $[Pt(CN)_2Tcbiim]^{2-}$ anion is shown in Fig. 1. Bond distances and angles are given in Tables III and IV respectively. The complex anion is approximately planar with only the nitriles of N4 and N5 and the C12 cyanide deviating slightly from the mean plane. There is how-

TABLE III. Interatomic Distances (Esd).

		N5′–C7′	1.151(12)
Pt–C11	1.915(9)	N4′–C6′	1.113(10)
Pt–C12	1.918(9)	N4–C6	1.143(11)
Pt–N1′	2.049(6)	N5–C7	1.134(10)
Pt–N1	2.077(6)	N9–C11	1.160(9)
N1–C5	1.350(9)	N10–C12	1.150(10)
N1–C2	1.366(9)	C5′–C4′	1.386(12)
N1′–C5′	1.353(9)	C5′–C7′	1.399(13)
N1′–C2′	1.377(10)	C4′–C6′	1.446(12)
N3′–C2′	1.319(9)	C2′–C2	1.442(11)
N3′–C4′	1.365(11)	C4–C5	1.391(11)
N3–C2	1.322(9)	C4–C6	1.429(12)
N3–C4	1.338(9)	C5–C7	1.408(11)

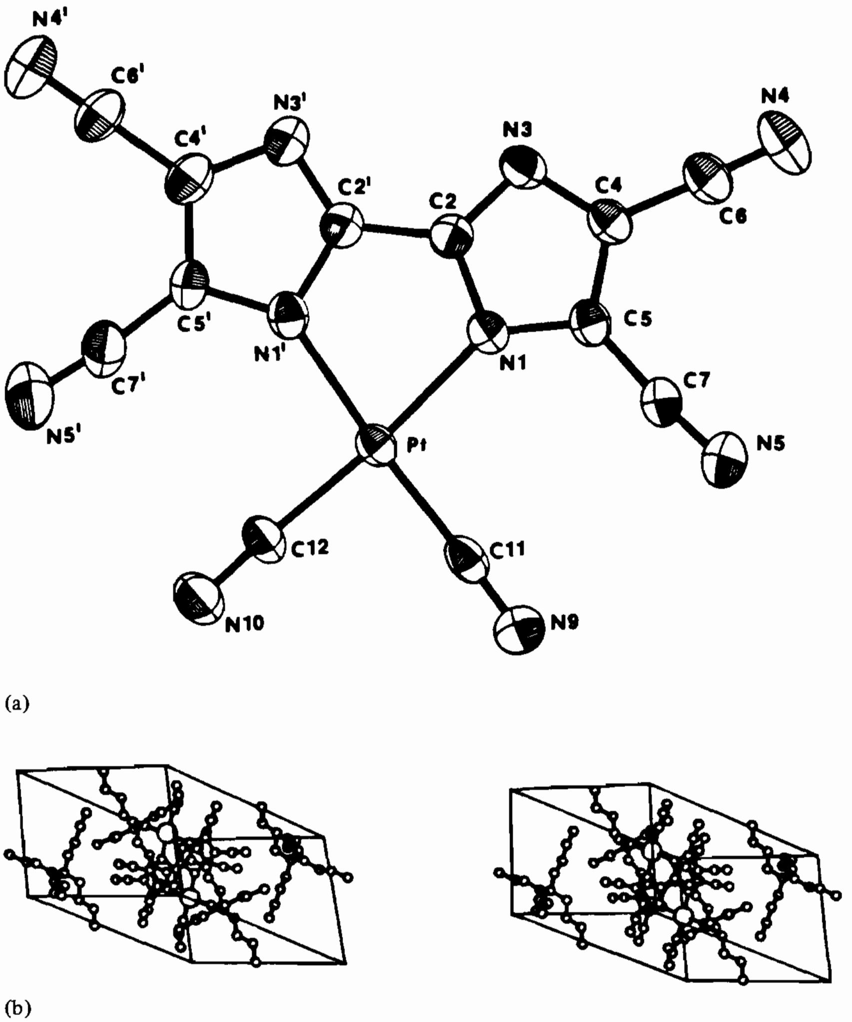

Fig. 1. (a) Structure of the platinum complex. (b) Stereoview of the molecule.

TABLE IV. Selected Interatomic Angles (Esd).

C11–Pt–C12	87.71(33)	C5'–C4'–C6'	125.23(90)
C11–Pt–N1'	175.65(30)	N3'–C2'–N1'	116.04(69)
C11–Pt–N1	97.01(27)	N3'–C2'–C2	128.63(79)
C12–Pt–N1'	96.32(30)	N1'–C2'–C2	115.31(69)
C12–Pt–N1	173.61(27)	N3–C2–N1	114.21(66)
N1'–Pt–N1	78.85(24)	N3–C2–C2'	130.52(75)
C5–N1–C2	104.55(63)	N1–C2–C2'	115.26(73)
C5–N1–Pt	139.75(53)	N3–C4–C5	111.06(69)
C2–N1–Pt	114.31(49)	N3–C4–C6	123.27(77)
C5'–N1'–C2'	103.29(64)	C5–C4–C6	125.63(80)
C5'–N1'–Pt	141.45(58)	N1–C5–C4	106.56(67)
C2'–N1'–Pt	115.19(48)	N1–C5–C7	125.47(74)
C2'–N3'–C4'	101.92(70)	C4–C5–C7	127.96(75)
C2–N3–C4	103.58(63)	N5'–C7'–C5'	174.7(11)
N1'–C5'–C4'	107.41(75)	N4'–C6'–C4'	179.5(34)
N1'–C5'–C7'	125.26(81)	N4–C6–C4	177.6(10)
C4'–C5'–C7'	127.32(79)	N5–C7–C5	174.78(96)
N3'–C4'–C5'	111.31(70)	N9–C11–Pt	176.63(75)
N3'–C4'–C6'	123.39(86)	N10–C12–Pt	177.62(84)

ever a slight folding of the anion as shown by the 10.5 dihedral angle between the plane of the $Pt(CN)_2$ moiety and the $Tcbiim^{2-}$ ligand.

The coordination around the platinum is distorted from square by the chelating ligand which makes an angle of 78.8 at platinum. This is very similar to that found for the isoelectronic anion $[Ir(CO)_2Tcbiim]^-$ [2]. The platinum–carbon distances (1.915–1.918 Å) are significantly shorter than those found in the typical salts of tetracyanoplatinates but the carbon–nitrogen distances in the cyanides are in the same range [6]. These facts suggest a slightly smaller pi accepting ability for $Tcbiim^{2-}$ compared to CN^- although the stability of the ion indicates a comparable *trans* effect since most ligands *trans* to cyanide are quite labile.

The size of the cation apparently prevents the stacking of the planar anions, although signs of intermolecular association do not appear in concentrated solutions of $(NH_4)_2[Pt(CN)_2Tcbiim]$ (which is quite soluble) as they do for salts of the iridium carbonyl analog. However if a solution of $BaCl_2$ is allowed to diffuse into a solution of *3*, long 'whiskers' form, which although not suitable for single crystal diffraction, do show powder X-ray patterns with strong lines corresponding to a 3.32 Å separation.

We made several attempts to prepare dimers in which $Tcbiim^{2-}$ was tetradentate to two platinum atoms, similar to dimers we have synthesized using iridium(I) and Cu(I) [3, 10]. The mixing of *cis*-$Pt(NH_3)_2(CN)_2$ in 1:1 ratio with *3* or in 2:1 ratio with $H_2Tcbiim$ leads to the formation of $Pt(CN)_2$. No reaction was observed between *3* and $Pt(CN)_2$ during lengthy reflux, although $Pt(CN)_2$ will slowly react with $Tcbiim^{2-}$ producing *3* in low yield. Mixing of *3* with $PtCl_4^{2-}$ followed by addition of two equivalents of CN^- leads to precipitation of $Pt(CN)_2$. Finally, $[Pt(COD)(acac)](BF_4)$ was refluxed in 2:1 ratio with $H_2Tcbiim$ in acetonitrile. This produced only *5* with no further addition of platinum complex. We conclude that the 'backside' of $Tcbiim^{2-}$ lacks sufficient basicity to bind Pt(II) when the 'frontside' is already bound to Pt(II). It is possible that such dimers might form, as they do in the case of Cu(II), [10] when other strong donors are present *e.g.* $[(dien)Cu(Tcbiim)Cu(dien)]^{2+}$ dien = diethylenetriamine but we do not presently know how to synthesize these analogs. It should also be noted that in the above remarks '$Pt(CN)_2$' does not represent a very tractable material. It is white, hard to filter, likely polymeric and is hydrated to an uncertain degree. This is quite different from the $Pt(CN)_2$ used in the preparation of *cis*-$Pt(NH_3)_2(CN)_2$ which is prepared from thermal decomposition of $(NH_4)_2[Pt(CN)_4]$ and which may also be polymeric but is orange and anhydrous [7].

TABLE V. Atomic Coordinates.

Pt	0.211040(18)	0.400738(27)	0.255731(25)
N1	0.26517(37)	0.57426(52)	0.36461(51)
N1′	0.25353(36)	0.45362(58)	0.15683(50)
N3′	0.32571(43)	0.60197(64)	0.14663(58)
N3	0.35781(42)	0.73012(56)	0.40334(59)
N5′	0.18189(72)	0.2171(10)	−0.11348(81)
N4′	0.31132(54)	0.50321(87)	−0.13318(72)
N4	0.42074(59)	0.91631(79)	0.68817(79)
N5	0.22549(64)	0.62838(80)	0.61187(75)
N9	0.15963(49)	0.33383(69)	0.41998(67)
N10	0.15054(50)	0.14150(73)	0.09011(69)
C5′	0.25059(50)	0.41671(77)	0.04994(65)
C4′	0.29500(53)	0.50686(89)	0.04494(75)
C2′	0.29808(48)	0.56629(72)	0.20911(65)
C2	0.31000(49)	0.62860(71)	0.32619(65)
C4	0.34294(51)	0.74296(68)	0.49569(69)
C5	0.28492(48)	0.64881(69)	0.47355(65)
C7′	0.21082(64)	0.3063(10)	−0.03738(82)
C6′	0.30461(54)	0.50491(87)	−0.05546(82)
C6	0.38467(60)	0.83963(81)	0.60285(85)
C7	0.25102(58)	0.63254(74)	0.54748(74)
C11	0.17712(45)	0.36136(68)	0.35793(71)
C12	0.17201(50)	0.23938(78)	0.15042(71)
N11	0.89210(37)	0.24095(52)	0.13875(49)
C13	0.80809(63)	0.2111(10)	0.14883(94)
C14	0.74973(68)	0.10292(95)	0.0670(11)
C15	0.67538(81)	0.0708(13)	0.0811(14)
C16	0.61800(88)	−0.0293(14)	0.0154(16)
C17	0.86500(64)	0.26166(89)	0.02887(79)
C18	0.93210(62)	0.29942(75)	0.00113(77)
C19	0.90180(92)	0.3280(11)	−0.0997(11)
C20	0.95967(94)	0.3551(14)	−0.1441(11)
C21	0.94455(63)	0.13784(89)	0.12616(88)
C22	0.96822(70)	0.09672(97)	0.21644(89)
C23	1.0284(10)	0.0082(11)	0.2125(13)
C24	1.0630(12)	−0.0283(14)	0.2953(12)
C25	0.94579(73)	0.34877(92)	0.23948(82)
C26	0.91631(69)	0.46293(83)	0.26149(88)
C27	0.9679(11)	0.56126(96)	0.3630(11)
C28	0.9515(11)	0.6757(10)	0.3945(13)
N12	0.62292(38)	0.76223(55)	0.38369(50)
C29	0.60602(51)	0.84006(75)	0.48693(69)
C30	0.66548(60)	0.83803(83)	0.59832(71)
C31	0.64544(72)	0.9261(11)	0.69670(85)
C32	0.6647(11)	1.0477(12)	0.7208(11)
C33	0.61883(50)	0.63268(71)	0.36775(64)
C34	0.53276(54)	0.57504(77)	0.35018(71)
C35	0.54144(58)	0.45359(84)	0.34965(82)
C36	0.45844(69)	0.38314(92)	0.3212(10)
C37	0.55415(51)	0.77770(72)	0.28591(67)
C38	0.56066(63)	0.71434(82)	0.17173(73)
C39	0.49460(65)	0.74525(88)	0.08295(77)
C40	0.50284(82)	0.6861(11)	−0.03084(88)
C41	0.71360(52)	0.79652(77)	0.39439(67)
C42	0.73393(58)	0.92277(82)	0.41109(78)
C43	0.82145(70)	0.93978(97)	0.40084(88)
C44	0.84715(82)	1.0670(12)	0.4263(11)

Attempts at oxidizing the salts of $[Pt(CN)_2Tcbiim]^{2-}$ in analogy to the preparation of the partially oxidized, anisotropic materials, have not so far been successful. These efforts have included aerial oxidation, electrolysis at controlled potential, and mixing with appropriate quantities of the oxidative addition compound formed with chlorine. Apparently the bonding strength of the stack which can form in this system is not sufficient to recoup the energy required for oxidation. This is surprising in view of the similarities of the electronic structure of Tcbiim^{2-} to cyanide and may be due to the greater ligand–ligand repulsions.

The synthetic aspects of tetracyanobiimidazole complexes of platinum are quite promising and offer potentially useful routes in several directions. The thermal decomposition of *3* analogous to the preparation of anhydrous Pt(CN)_2 should lead to a similarly useful starting material. This method would circumvent the problems which the preparation of *cis* compounds of strong *trans* directors typically present. The formation of *5* suggests that other neutral ligands of low electronegativity would also be compatible with the Pt(Tcbiim) moiety and the possible preparation of $\text{Pt(L)}_2\text{Tcbiim}$ derivatives by substitution reactions. These reaction pathways are under further investigation in our laboratory.

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Supplementary Information

Tables of structure factors, anisotropic thermal parameters, and least squares planes are available upon request to either of the senior authors (25 pages).

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