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Inorganica Chimica Acta 265 (1997) 267–270

Inorganica Chimica Acta

Note

Bifunctional activation of cyanoguanidine. Synthesis and molecular structure of the azametallacycle *cis*-[(PPh$_3$)$_2$Pt{NHC(OMe)=NC(NH$_2$)=NH}][BPh$_4$]

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Received 10 March 1997; accepted 29 April 1997

Abstract

The cyanoguanidine complex *cis*-[Pt{NCNC(NH$_2$)$_2$}$_2$(PPh$_3$)$_2$][BPh$_4$]$_2$, prepared by reacting *cis*-[PtCl$_2$(PPh$_3$)$_2$] with cyanoguanidine in the presence of Na[BPh$_4$], readily reacts with methanol to give *cis*-[(PPh$_3$)$_2$Pt{NHC(OMe)=NC(NH$_2$)=NH}][BPh$_4$] containing a novel type of azametallacycle whose molecular structure is established by X-ray crystallography. Its formation involves metal-promoted nucleophilic addition of the alcohol to the cyano group of a cyanoguanidine ligand, combined with deprotonation of the guanidine unit which then chelates the Pt(II) centre. © 1997 Elsevier Science S.A.

Keywords: Crystal structures; Platinum complexes; Cyanoguanidine complexes; Azametallacycle complexes

1. Introduction

Cyanoguanidine (or dicyandiamide, with tautomeric forms N≡C–N=C(NH$_2$)$_2$ and N≡C–NHC(=NH)NH$_2$), the dimeric form of cyanamide (a recently recognised nitrogenase substrate [1]), is a polyfunctional species, containing both the cyano and the guanidine groups. It has commercial and biological significance, being a precursor for the synthesis of some organonitrogen compounds [2]. Its common mode of coordination to a metal is 'end-on' through the cyano moiety [3–7], but the coordination of the guanidine fragment, or one of its derivatives, has yet to be explored. Moreover, guanidine complexes are barely known [8,2a] in spite of their possible [9–11] relevance to the investigation of some biological systems.

In this study we report that a Pt(II) centre activates cyanoguanidine towards nucleophilic attack at the cyano group and also promotes mono-deprotonation of the guanidine moiety which then chelates the metal ion forming an unprecedented type of azametallacycle. The molecular structure of the complex has been determined by X-ray diffraction analysis.

2. Results and discussion

Treatment of a tetrahydrofuran (THF) solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with cyanoguanidine in the presence of Na[BPh$_4$] (both in a four-fold molar ratio relative to the complex) affords the dicyanoguanidine complex *cis*-[Pt{N≡CN=C(NH$_2$)$_2$}$_2$(PPh$_3$)$_2$][BPh$_4$]$_2$ (1). This intermediate, in acetone or CH_2Cl_2, upon reaction with MeOH, at ambient temperature, rapidly forms the azametallacycle species *cis*-[(PPh$_3$)$_2$Pt{NHC(OMe)=NC(NH$_2$)=NH}]-

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PII S0020-1693(97)05636-3

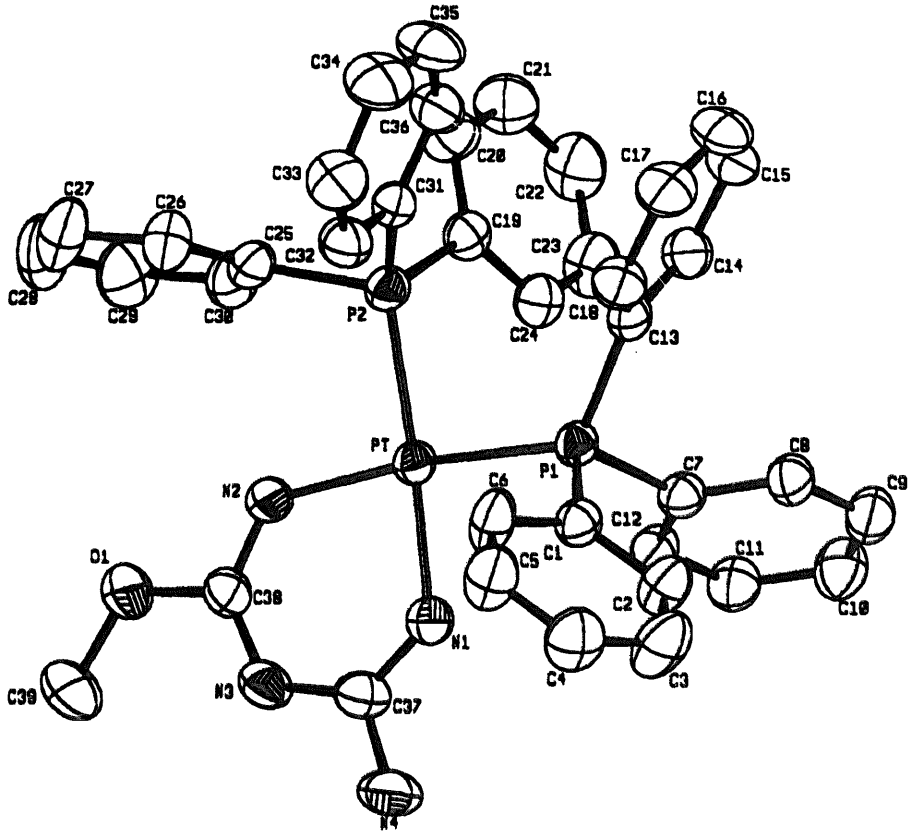


Fig. 1. View of the *cis*-$[(PPh_3)_2Pt\{NHC(OMe)=NC(NH_2)=NH\}]^+$ cation with atom numbering scheme.

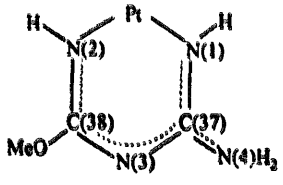
$[BPh_4]$ (**2**) (reaction (1)) with loss of one of the cyanoguanidine ligands.

cis-$[[PtN{\equiv}CN{=}C(NH_2)_2]_2(PPh_3)_2][BPh_4]_2$
(**1**)

MeOH
⇒ *cis*-$[(PPh_3)_2Pt\{NHC(OMe)=NC(NH_2)=NH\}][BPh_4]$
(**2**)
(1)

Both compounds **1** and **2** were isolated (~40–50% yields) as white solids and characterised by elemental analyses, IR, ^1H, ^{31}P and ^{13}C NMR spectroscopies. The X-ray crystal structure of **2** was also determined, and the molecular structure of the cationic complex is shown in Fig. 1, and selected bond distances and angles are given in Table 1.

The platinum ion, which shows the typical square-planar coordination geometry, is bonded to a novel type of azametallacyclic ligand comprising the Pt atom and the skeleton of the guanidine. The best mean plane calculated with the guanidine atoms N(2), C(38), N(3), C(37), N(1) shows planarity of this system (range of deviations from −0.007(8) to 0.004(7) Å) with the platinum ion −0.0356(8) Å out of this plane. The hexatomic ring can then be described as a delocalised π-electron system, as shown in **a**, involving also the $N(4)H_2$ amino group thus accounting for the shorter N(3)–C(38) bond length, 1.31(1) Å, compared with that of the adjacent N(3)–C(37) bond, 1.34(1) Å. The two Pt–N bond distances, Pt–N(1) 2.048(6) Å and Pt–N(2) 2.032(7) Å, are not significantly different and are consistent with those reported [11,12] for other Pt(II) complexes with substituted-guaninate or -guanine ligands.



(a)

Its ^{13}C NMR spectra (both ^1H-coupled and ^1H-decoupled ones) show two singlets at δ 159.7 and 158.0 ppm (in DMSO-d_6), assigned to the two carbon atoms of the metallacycle ring. As expected for the *cis*-geometry of **2**, the $^{31}P\{^1H\}$ NMR spectrum exhibits an AB pattern, consisting of two doublets centred at δ_A 15.4 and δ_B 10.5 ppm relative to H_3PO_4, with the expected ^{195}Pt satellites ($^1J(P_APt)$ 3218.6 Hz and $^1J(P_BPt)$ 3176.8 Hz).

The formation of the azametallacycle complex **2** involves the overall activation, at ambient temperature, by the Pt(II) centre at complex **1**, of a cyanoguanidine ligand towards both (i) nucleophilic addition, by MeOH, at the cyano group, and (ii) deprotonation at the guanidine group.

Reaction (i) is consistent with the significant increase in the IR spectrum of ν(N≡C) of cyanoguanidine upon coordination, i.e. from 2180–2140 cm^{-1} in the free species to

Table 1
Selected bond distance (Å) and angles (°) for *cis*-[(PPh$_3$)$_2$Pt{NHC(OMe)=NC(NH$_2$)=NH}][BPh$_4$]·0.25CH$_3$COCH$_3$

Pt–P(1)	2.283(2)	Pt–P(2)	2.271(2)
Pt–N(1)	2.048(6)	Pt–N(2)	2.032(7)
P(1)–C(1)	1.841(8)	P(1)–C(7)	1.835(6)
P(1)–C(13)	1.811(8)	P(2)–C(19)	1.811(8)
P(2)–C(25)	1.847(7)	P(2)–C(31)	1.812(8)
N(1)–C(37)	1.29(1)	N(2)–C(38)	1.29(1)
N(3)–C(37)	1.34(1)	N(3)–C(38)	1.31(1)
N(4)–C(37)	1.35(1)	O(1)–C(38)	1.35(1)
O(1)–C(39)	1.43(1)		
N(1)–Pt–N(2)	85.7(3)	P(2)–Pt–N(2)	90.9(2)
P(2)–Pt–N(1)	176.5(2)	P(1)–Pt–N(2)	172.4(2)
P(1)–Pt–N(1)	86.7(2)	P(1)–Pt–P(2)	96.7(1)
Pt–N(1)–C(37)	128.2(5)	Pt–N(2)–C(38)	126.3(6)
C(37)–N(3)–C(38)	122.5(8)	C(38)–O(1)–C(39)	118.4(8)
N(3)–C(37)–N(4)	114.5(8)	N(1)–C(37)–N(4)	118.8(7)
N(1)–C(37)–N(3)	126.8(8)	N(3)–C(38)–O(1)	117.2(8)
N(2)–C(38)–O(1)	112.3(7)	N(2)–C(38)–N(3)	130.5(7)

2200 cm^{-1} (with a shoulder at 2250 cm^{-1}) in complex **1**, indicating a predominance of the σ-electron release of the cyanoguanidine to the Pt(II) centre relative to the π-electron backbonding component of the bond, with resulting activation of this ligand to nucleophilic attack, a type of reaction well documented [13] for organonitriles. The mild conditions and the speed of reaction (i) contrast with those required [2b] for the other metal ion-mediated additions of alcohols to cyanoguanidine.

Reaction (ii) reflects the enhancement of the acidity of cyanoguanidine upon coordination, whereas the conceivable proton acceptance by the guanidine group of the second cyanoguanidine molecule is in accord with the known [9] very strong basic character of guanidines.

This bifunctional activation of cyanoguanidine by coordination results in structural and electronic rearrangements which are favourable to metal-binding of the ligand through both the cyano-derived and the guanidine-derived groups, with formation of the chelate complex **2** in which the chelating nitrogen-ligand is a formally monoanionic ligand.

The observed coordination behaviour of the guanidine group can possibly be of significance for its binding ability in inorganic and biological systems.

3. Experimental

The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] was prepared according to a published method [14], whereas the other reagents were purchased from Aldrich.

All reactions were carried out under dinitrogen, through standard vacuum and inert gas flow techniques. The solvents were dried by standard procedures and freshly distilled before use. IR spectra were recorded on a Perkin-Elmer 683 spectrophotometer and NMR spectra on a Varian Unity 300 spectrometer.

3.1. Syntheses

3.1.1. *Cis*-[Pt{N≡CN=C(NH$_2$)$_2$}$_2$(PPh$_3$)$_2$][BPh$_4$]$_2$ (1)

A suspension of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.15 g, 0.19 mmol) with NCNC(NH$_2$)$_2$ (0.063 g, 0.76 mmol) and Na[BPh$_4$] (0.26 g, 0.76 mmol) in THF (30 cm^3) was stirred for 5 days. The solution was then separated from the white solid by filtration and taken to dryness. Extraction with CH_2Cl_2 (~8 cm^3) followed by filtration, concentration in vacuo and addition of Et_2O led to the formation of a pale yellow oil which was separated from the solution by decantation. Addition of Et_2O to this oily residue, followed by freezing in liquid nitrogen and leaving to warm to room temperature with vigorous stirring, resulted in the separation of a white solid which was filtered off, washed with Et_2O and dried in vacuo. Recrystallisation from CH_2Cl_2/Et_2O gave complex **1** as a white solid which was washed with Et_2O and dried in vacuo (~40% yield). IR (KBr pellet, cm^{-1}): ν(NH) 3460 (m,br), 3380 (m,br), 3060 (m,br), 3000 (m,br); ν(N≡C) 2250 (sh), 2200 (s,br); δ(NH) or ν(N=C) 1625 (s), 1580 (sh), 1550 (s, br), ~1500 (s). ^{13}C NMR (CD_2Cl_2, δ, ppm): 160.81 (s, NCN*C*(NH$_2$)$_2$), 131.19 (s, N*C*NC(NH$_2$)$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm rel. H_3PO_4): 3.5 (s, J(^{31}P^{195}Pt) = 3615.7 Hz). *Anal.* Calc. for $C_{88}H_{78}N_8P_2B_2Pt \cdot 3/5CH_2Cl_2$: C, 67.5; H, 5.0; N, 7.1. Found: C, 67.3; H, 4.9; N, 7.1%.

3.1.2. *Cis*-[(PPh$_3$)$_2$Pt{NHC(OMe)=NC(NH$_2$)=NH}][BPh$_4$] (2)

Methanol (1 cm^3) was added to a solution of complex **1** (0.14 g, 0.092 mmol) in CH_2Cl_2 (20 cm^3). Filtration of the reaction solution followed by concentration in vacuo and addition of Et_2O resulted in the formation of an oil which was separated off by decantation. Et_2O was added again (10 cm^3) and the system was stirred, frozen in liquid nitrogen, left warming until room temperature and stirred again giving a white solid of complex **2** which was filtered off and dried in vacuo (~50% yield). Recrystallisation from CH_2Cl_2/n-pentane afforded a crystalline material. The sample which was analysed by X-ray diffraction was obtained upon recrystallisation from acetone/methanol. IR (KBr pellet, cm^{-1}): ν(NH) 3420 (m), 3330 (m); δ(NH) or ν(N=C) 1700 (m), 1620 (m), 1570 (s), 1510 (m). ^{13}C NMR (DMSO-d$_6$, δ, ppm): 159.68 (s, br, NHC(OCH$_3$)=N*C*(NH$_2$)=NH), 54.24 (s, O*C*H$_3$). ^{31}P{^{1}H} NMR (DMSO-d$_6$, δ, ppm rel. H_3PO_4): 15.6 (d, ^2J(^{31}P^{31}P) = 25.1 Hz, J(^{31}P^{195}Pt) = 3218.6 Hz), 10.5 (d, ^2J(^{31}P^{31}P) = 25.1 Hz, J(^{31}P^{195}Pt) = 3176.8 Hz). *Anal.* Calc. for $C_{63}H_{57}N_4OP_2BPt \cdot 1/4CH_2Cl_2$: C, 64.6; H, 4.9; N, 4.8. Found: C, 64.6; H, 4.7, N, 3.4%.

3.1.3. *Crystal data for cis-*[(PPh$_3$)$_2$Pt{NH–C(OMe)=NC(NH$_2$)=NH}][BPh$_4$]·0.25CH$_3$COCH$_3$

$C_{63.5}H_{57.5}BP_2N_4O_{1.25}Pt$, MW = 1167.5, triclinic $P\bar{1}$, a = 12.323(3), b = 15.808(4), c = 16.972(3) Å, α = 93.15(4), β = 106.11(3), γ = 111.73(4)°; V = 2904(1) Å^3, Z = 2, D_c = 1.34 Mg m^{-3}; λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 25.15 cm^{-1}, F(000) = 1182, T = 295 K.

A prismatic (white) crystal of dimensions 0.38 × 0.42 × 0.58 mm was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 (Febo System) [15] diffractometer with graphite-monochromated (Mo Kα) radiation ($\lambda = 0.71069$ Å). The orientation matrix and preliminary unit-cell dimensions were determined from 25 reflections found by mounting the crystal at random. For the determination of precise lattice parameters, 30 strong reflections with $9 \leq \theta \leq 14°$ were used. Integrated intensities for *hkl* reflections were measured in the interval $\theta = 2.5$–$26°$, using $\theta/2\theta$ scans. Two standard reflections, −1, 5, 3 and −3, 1, 1 were collected every 200 reflections. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz–polarisation effects and for absorption as described by North et al. [16].

The structure was solved by heavy atoms methods [17]. Refinement was carried out by full-matrix least-squares; the function minimised was $\Sigma w(F_o^2 - F_c^2)^2$, with weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 6.71P]$, where $P = \max(F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters except the atoms of the clathrated acetone molecule. The H atoms were placed in calculated positions with fixed, isotropic thermal parameters ($1.2U_{eq}$ of the parent carbon atom). Conventional $R = 0.0473$, based on F values of 9076 reflections having $F_o^2 \geq 3\sigma(F_o)^2$ and $S = 1.216$ (wR on $F^2 = 0.128$). Structure refinement was carried out with SHELXL-93 [18] using the scattering factors enclosed therein; the drawing was produced using ORTEP II [19]. Selected bond lengths and angles are given in Table 1.

4. Supplementary material

Atomic coordinates, bond lengths and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

5. Note added in proof

After the manuscript had been submitted for publication, a paper appeared (D.P. Fairlie, W.G. Jackson, B.W. Skelton, H. Wen, A.H. White, W.A. Wickramasinghe, T.C. Woon and H. Taube, Inorg. Chem., 36 (1997) 1020) on the activation of dimethylcyanamide, by coordination to some Pt(II), Co(II) or Os(II) centres, towards amination and hydration to form amidine or urea ligands, respectively, aiming to develop models for arginine–metal binding.

Acknowledgements

This work has been partially supported by JNICT, the PRAXIS XXI programme (Portugal), and the JNICT/CNR (Italy) collaboration programme.

References

[1] R.W. Miller and R.R. Eady, Biochim. Biophys. Acta, 952 (1988) 290.
[2] (a) P. Rây, Chem. Rev., 61 (1961) 313; (b) R.K. Ray, M.K. Bandyopadhyay and G.B. Kauffman, Polyhedron, 8 (1989) 757; (c) V.H. Michaud, W. Gole, B. Hammer, J.V. Seyerl, W. Sturm, S. Weiss and R. Youngman, Chem.-Z., 112 (1988) 287.
[3] (a) M.F.N.N. Carvalho, A.J.L. Pombeiro, A. Hills, D.L Hughes and R.L. Richards, J. Organomet. Chem., 469 (1993) 179; (b) M.F.C. Guedes da Silva, E.M.P.R.P. Branco, Y. Wang, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, R. Bertani, R.A. Michelin, M. Mozzon, F. Benetollo and G. Bombieri, J. Organomet. Chem., 490 (1995) 89.
[4] (a) M.J. Begley, P. Hubberstey and P.H. Walton, J. Chem. Soc., Chem. Commun., (1989) 502; (b) M.J. Begley, P. Hubberstey and C.H.M. Moore, J. Chem. Res. S, (1985) 378; (c) P. Hubberstey and C.P. Falshaw, J. Chem. Res. S, (1982) 176.
[5] (a) A. Chiesi, L. Coghi, A. Mangia, M. Nardelli and G. Pelizzi, Acta Crystallogr., Sect B, 27 (1971) 192; (b) A. Chiesi Villa, L. Coghi, A. Mangia, M. Nardelli and G.J. Pelizzi, Cryst. Mol. Struct., 1 (1971) 291; (c) A. Chiesi Villa, L. Coghi, A. Manfredotti and C. Guastini, Cryst. Struct. Commun., 3 (1974) 739.
[6] L. Coghi, A. Mangia, M. Mandelli, E. Pelizzi and L. Sozzi, J. Chem. Soc., Chem. Commun., (1968) 475.
[7] H. Fischer, F. Seitz and G. Müller, J. Organomet. Chem., 320 (1987) 185.
[8] R.C. Mehrotra, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), Comprehensive Coordination Chemistry, Vol. 2, Pergamon, New York, 1987, p. 269.
[9] D.P. Fairlie and W.G. Jackson, Inorg. Chem., 29 (1990) 140.
[10] E.M.A. Ratilla and N.M. Kostic, J. Am. Chem. Soc., 110 (1988) 4427.
[11] G. Frommer, I. Mutikainen, F.J. Pesch, E.C. Hillgeris, H. Preut and B. Lippert, Inorg. Chem., 31 (1992) 2429.
[12] G. Schröder, J. Kozelka, M. Sabat, M.-H. Fouchet, R. Beyerle-Pfnür and B. Lippert, Inorg. Chem., 35 (1996) 1647.
[13] R.A. Michelin, M. Mozzon and R. Bertani, Coord. Chem. Rev., 147 (1996) 299.
[14] J.C. Bailar, Jr. and H. Itatani, Inorg. Chem., 4 (1965) 1618.
[15] D. Belletti, FEBO, a new hardware and software system for controlling a Philips PW1100 single crystal diffractometer, Internal Rep. 1/93, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, 1993.
[16] A.C.T. North, D.C. Phillips and F.S. Mathews, Acta Crystallogr., Sect. A, 24 (1968) 351.
[17] G.M. Sheldrick, SHELXS86, Acta Crystallogr., Sect. A, 46 (1990) 467.
[18] G.M. Sheldrick, SHELXS93, program for the refinement of crystal structures, University of Göttingen, Germany.
[19] C.K. Johnson, ORTEP II, Rep. ORNL-5138, Oak Ridge National Laboratory, TN, USA, 1976.