In summary, we can conclude that the three-dimensional energy surface for acid-catalyzed hydration–dehydration is such that relatively small variations in structure can result in significant changes in the position of the transition state. The same reaction mechanism, however, is in operation whether the aldehyde has a large tendency to hydrate, as with formaldehyde, or little tendency to hydrate, as with benzaldehydes.

Experimental Section

3,5-Dinitrobenzaldehyde was a gift of Professor P. Yates. All other aldehydes were commercially available. The hydration equilibrium constant for 3,5-dinitrobenzaldehyde was measured by using the method of Bell and Sorenson.[9]

Rate constants were measured by using a Durrum-Gibson stopped-flow spectrophotometer. The aldehyde dissolved in 0.1 M NaOH–0.5 M NaCl was mixed in the spectrophotometer with solutions containing 0.1 M HCl, buffer, and NaCl such that the total ionic strength was also 0.6. The wavelength maximum of the aldehyde was monitored. The photomultiplier output was digitized and the digital data were transferred to a Tektronix 4050 minicomputer. A total of 118 data points were obtained in each kinetic run. First-order rate constants were calculated by using the infinity method [$\ln (A_\infty - A_t)$ vs. t] in most cases, with the Guggenheim method being used for runs with a half-life greater than 5 s. For each solution, five to nine separate kinetic runs were carried out, and the rate constnats were calculated as the average of these.

Acknowledgment. Continued financial support from the Natural Sciences and Engineering Research Council of Canada is greatefully acknowledged.

Registry No. H_3O^+, 13968-08-6; H_2O, 7732-18-5; OH^-, 14280-30-9; $CH_2CNCOOH$, 372-09-8; $CH_2ClCOOH$, 79-11-8; $CH_2OMeCOOH$, 625-45-6; HCOOH, 64-18-6; $Cl(CH_2)_3COOH$, 627-00-9; CH_3COOH, 64-19-7; CH_2CNCOO^-, 23297-32-7; CH_2ClCOO^-, 14526-03-5; $CH_2OMeCOO^-$, 20758-58-1; $HCOO^-$, 71-47-6; $Cl(CH_2)_3COO^-$, 75974-45-7; CH_3COO^-, 71-50-1; $H_2PO_4^-$, 14066-20-7; HPO_4^{2-}, 14066-19-4; $CCl_3PO_3H^-$, 59641-42-8; $CHCl_2PO_3H^-$, 57556-34-0; $CH_2ClPO_3H^-$, 54947-16-9; $CH_2OHPO_3H^-$, 62305-76-4; $CH_3PO_3H^-$, 39863-50-8; $(CH_3)_2AsO_2H$, 75-60-5; hydrogen sulfite, 15181-46-1; 3,5-dinitrobenzaldehyde, 14193-18-1; 4-chloro-3-nitrobenzaldehyde, 16588-34-4; 4-nitrobenzaldehyde, 555-16-8; 3-nitrobenzaldehyde, 99-61-6; 4-(trifluoromethyl)benzaldehyde, 455-19-6; 3-chlorobenzaldehyde, 587-04-2; 4-chlorobenzaldehyde, 104-88-1; 4-chlorobenzaldehyde hydrate, 54365-48-9; 3-chlorobenzaldehyde hydrate, 85152-57-4; 4-(trifluoromethyl)benzaldehyde hydrate, 85152-58-5; 3-nitrobenzaldehyde hydrate, 85152-59-6; 4-nitrobenzaldehyde hydrate, 55649-04-2; 4-chloro-3-nitrobenzaldehyde hydrate, 85152-60-9; 3,5-dinitrobenzaldehyde hydrate, 85152-61-0.

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(36) The mathematical analyses suggested by Jencks and Jencks[21] are difficult here since ρ is not proportional to carbon–oxygen bond formation and cleavage. An important parameter is also missing, the direct correlation coefficient $\partial\rho/\partial\sigma$. A nonzero value for this corresponds to a curved Hammett plot. We feel that the substituent range is not sufficiently large to determine if such curvature exists.

N,N′-Dinitrosation of Pt(IV)-Coordinated 1,2-Ethanediamine: Crystal and Molecular Structure of Chloronitro(bipyridyl)(*N*,*N*′-dinitroso-1,2-ethanediaminato)-platinum(II) Hemihydrate

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Abstract: A Pt(IV) complex of the previously unknown ligand, the dianion of *N*,*N*′-dinitroso-1,2-ethanediamine, was synthesized by nitrosation of coordinated 1,2-ethanediamine and characterized by X-ray crystallography and ^{13}C NMR spectroscopy. $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ gives monoclinic crystals with a = 11.739 (4) Å, b = 7.332 (2) Å, c = 19.423 (6) Å, and β = 102.55 (2)° in space group $P2_1/c$. The structure was solved by the heavy atom method and refined by least-squares methods to a conventional R factor of 0.058 for 2268 observed data. In the crystal, one of the *N*-nitroso groups is syn and the other is anti to the carbon atoms of the five-membered en chelate ring, and the N–O distances in the N-coordinated nitro group differ greatly (1.278 (20) Å and 1.130 (19) Å). In the ^{13}C NMR spectrum, every carbon atom gives a different signal.

Primary amines coordinated to Pt(IV) can be N-nitrosated by treatment in aqueous solution with alkali metal nitrites,[1-3] an interesting reaction that has not been extensively studied. Complexes of this type may be of special interest because of the notorious carcinogenicity of many *N*-nitrosamines. This paper reports the N,N′-dinitrosation of Pt(IV)-coordinated 1,2-ethanediamine (en). The result is a complex of the new ligand $(ONNCH_2CH_2NNO)^{2-}$.

Experimental Section

Synthesis. *trans*-Dichloro(bipyridyl)(1,2-ethanediamine)platinum(IV) chloride pentahydrate, $[Pt(bpy)(en)Cl_2]Cl_2\cdot 5H_2O$, was prepared from $[Pt(bpy)(en)]Cl_2$ according to the method of Morgan and Burstall.[4] Two grams (3.11×10^3 mol) of it was dissolved in 20 mL of boiling water. To this was added 0.794 g (9.33×10^3 mol) of KNO_2 dissolved in 10 mL of boiling water. There was an immediate precipitation of an orange solid. The mixture was kept on the steam bath for 3 h. After the mixture cooled to room temperature, the precipitate was filtered off and washed with hot water, ethanol, and then ether. It was dissolved in boiling *N*,*N*′-dimethylformamide and recrystallized by cooling and evaporation. It decomposed explosively at 210 °C. Yield: 1.45 g (84%). Anal. Calcd for $[Pt(C_{10}H_8N_2)(C_2H_4N_4O_2)ClNO_2]\cdot 0.5H_2O$: C, 25.84; H, 2.35; N,

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(1) Cherngaev, I. I.; Adrianova, O. N.; Leites, N. Sh. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1961**, *6*, 252–253.

(2) Adrianova, O. N.; Gladkaya, N. Sh.; Vorotnikova, V. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1970**, *15*, 1278–1280.

(3) Adrianova, O. N.; Gladkaya, A. Sh.; Shchelokov, R. N. *Koord. Khim.* **1979**, *5*, 255–262.

(4) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1934**, 965–971.

0002-7863/83/1505-2725$01.50/0

17.38; Pt, 34.97; Cl, 6.36. Found: C, 26.46; H, 2.33; N, 17.31; Pt, 35.21; Cl, 6.66.

This substance is insoluble in water, alcohol, and ether. It dissolves in hot concentrated HCl. Evaporation of such a solution gives a yellow water-insoluble solid. Anal. Calcd. for $PtC_{12}H_{18}N_5Cl_3O_3$: C, 24.78; H 3.11; N, 12.04; Cl, 18.28; Pt, 33.53. Found: C, 24.56; H 3.33; N, 11.77; Cl, 18.23; Pt, 33.45.

Spectra. Proton-decoupled ^{13}C NMR spectra were taken on a Varian 80-MHz FT NMR at probe temperatures (~40 °C). For $[Pt(bpy)(en)Cl_2]Cl_2$ the sample was a saturated D_2O solution and chemical shifts were referred to external Me_4Si. For $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ the sample was a saturated DMF solution and chemical shifts were referred to the methyl carbon peaks of that solvent. In both cases a D_2O lock was used (to external D_2O in the latter), and pulse width was 4 μs, pulse delay 0 s, and acquisition time 0.5 s.

Infrared spectra was taken as KBr discs on a Beckman Model 621 IR spectrophotometer.

Collection of Diffraction Data and Solution of Structure. Preliminary precession photographs on several crystals established the monoclinic system (Laue symmetry $2/m$) and the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The space group $P2_1/c$ was thus indicated. Data collection was carried out by using a Nicolet P3/F automatic diffractometer equipped with a graphite-crystal monochromator. Preliminary θ–2θ scans on high-intensity reflections from several different crystals showed that most crystals were of low quality. A fairly good crystal was mounted and satisfactory lattice parameters were determined by least-squares procedures using the angular positions of 25 independently centered reflections well separated in reciprocal space. A data set, collected by θ–2θ scans using Mo Kα radiation and totaling 2554 absorption-corrected unique reflections (out to 2θ of 55°) with $F > 2.5\sigma(F)$, was gathered on this crystal. The net intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied.[5]

The locations of the Pt atom and the Cl atom were apparent from a Patterson synthesis. A difference Fourier synthesis phased by these two atoms gave the locations of all of the other non-hydrogen atoms except the partial occupancy water of crystallization which was added in a later stage. Refinement proceeded with conversion to anisotropic thermal parameters and insertion of riding hydrogen-atoms in positions calculated (assuming $d_{C-H} = 0.96$ Å). Each hydrogen atom's isotropic thermal parameter was allowed to vary independently. Neutral atom scattering factors from Cromer and Mann[6] were used for all non-hydrogen atoms and the scattering factors of Stewart et al.[7] were used for the hydrogen atoms. This solution and refinement used the SHELXTL series of programs[8] and gave the qualitative structure with $R_F = 7.59$, $R_{wF} = 7.98$. The results were judged not acceptable in detail; the standard deviations of bond distances and angles were high. The low quality of the other crystals (typical 2θ width 1.75–2.0°) suggested collection by ω scans of equivalent data and averaging. Data collection was therefore repeated by using this strategy. A new crystal of somewhat higher quality was ultimately found and centered with extreme care. A hemisphere of data was collected ($\pm h,k,\pm l$), out to 2θ of 58°. The same range of scan rates (3.91–29.30 deg/min) was used as in the θ–2θ data collection, but the width of the necessary scan was now only 1.5° rather than 2.5–2.7°. Thus more reflections were collected per hour, and the ω scan data set required but little more time to accumulate than the θ–2θ data set. The R(merge) for the averaging of the equivalent reflections was 0.055. The intensities of three standard reflections measured every 93 reflections showed no evidence of crystal decay. Other details of this second data collection and reduction as well as the crystal parameters, which were redetermined on the second crystal, are given in Table I. The structural model arrived at with the first set of data was adopted and refined, leading to the more satisfactory results given in the tables.

One hydrogen atom was refined independently in the final model. The other 11 were held as riding H's. All had their isotropic thermal parameters varied independently.

Table I. Experimental Data for the X-ray Diffraction Study on $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]\cdot 0.5H_2O$

a 11.739 (4) Å	
b 7.332 (2) Å	
c 19.423 (6) Å	
β 102.55 (2)°	
V 1631.8 (8) Å^3	
space group	$P2_1/c$ no. 14
Z	4
M_r	557.83
ρ(calcd)	2.277 g/cm^3
ρ(obsd)	2.25 g/cm^3
F_{000} 1040 e$^-$	
radiation	Mo Kα (λ = 0.710 69 Å)
absorption coeff	μ(Mo Kα) 92.8 cm^{-1}
crystal shape	irregular fragment
scan type	ω scans
scan speed	variable 3.91–29.30 deg min^{-1}
scan range	0.75° below ω to 0.75° above
background counting time	0.5(scan time)
reflections measd	$\pm h,k,\pm l$
max 2θ	58.0°
reflections collected systematic absences	9668 including 312 standards and 659 these gave 4324 unique data
unique data used	2268 with $F_o^2 > 2.5\sigma(F_o^2)$
$R_F\ \dfrac{\Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert}{\Sigma \lvert F_o\rvert}$	0.0585
$R_{wF}\ \left(\dfrac{\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2}{\Sigma w \lvert F_o\rvert^2}\right)^{1/2}$	0.0507
no. of variables	250
goodness of fit $\left(\dfrac{\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2}{m-n}\right)^{1/2}$	1.50
$w^{-1} = (\sigma(F)^2 + \lvert g\rvert F_o^2)$ where $g = 0.0000$	

Table II. Final Positional Parameters (×10^4) for Non-Hydrogen Atoms in $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$

atom	x	y	z
Cl	2125 (3)	−2088 (5)	584 (2)
N(1)	2581 (10)	−880 (18)	2185 (6)
C(1)	1624 (12)	−2151 (23)	2204 (9)
C(2)	521 (12)	−1005 (19)	1987 (7)
N(2)	685 (9)	218 (17)	1420 (6)
N(3)	3297 (13)	−538 (26)	2767 (7)
N(4)	−124 (11)	1369 (22)	1161 (6)
O(1)	−1068 (8)	1188 (20)	1357 (6)
O(2)	3987 (10)	750 (20)	2781 (6)
N(11)	3991 (7)	773 (17)	1153 (5)
C(21)	4117 (11)	1823 (18)	575 (7)
C(31)	5247 (12)	2041 (22)	441 (8)
C(41)	6160 (12)	1221 (21)	845 (8)
C(51)	6020 (13)	104 (21)	1418 (9)
C(61)	4913 (11)	−37 (21)	1516 (9)
N(12)	2058 (8)	2144 (16)	379 (5)
C(22)	3039 (10)	2605 (18)	168 (7)
C(32)	2988 (13)	3679 (20)	−447 (8)
C(42)	1947 (12)	4358 (25)	−787 (8)
C(52)	946 (14)	3852 (22)	−591 (7)
C(62)	997 (12)	2698 (22)	−11 (8)
N(5)	2503 (11)	2939 (21)	1848 (8)
O(3)	1895 (10)	3027 (18)	2319 (6)
O(4)	3113 (11)	4042 (15)	1741 (7)
Pt	2319 (1)	566 (2)	1285 (1)
Aq	4557 (20)	5935 (28)	951 (12)

Discussion

Primary amines ordinarily cannot be N-nitrosated. However, coordination and deprotonation of a primary amine make it formally resemble a secondary amine. The acidity of amine protons in high oxidation state metal complexes is, of course, well-known; many deprotonated complexes have even been isolated.[9–14] This N-nitrosation reaction therefore almost certainly

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[5] "Nicolet P3/F R3 Operations Manual"; Nicolet XRD Corp.; Cupertino, CA, 1979.

[6] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

[7] Stewart, R. F.; Davidson, E.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[8] Sheldrick, G. M. "Nicolet SHELXTL Operations Manual"; Nicolet XRD Corp.: Cupertino, CA, 1981.

[9] Watt, G. W.; Upchurch, D. G. *J. Am. Chem. Soc.* **1965**, *87*, 4212.

[10] Watt, G. W.; Upchurch, D. G. *J. Am. Chem. Soc.* **1967**, *89*, 177.

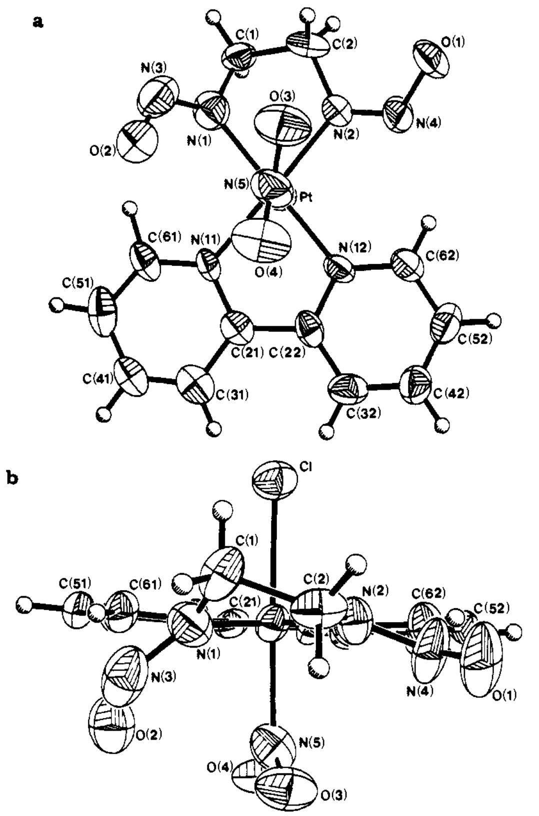

Figure 1. Two perspective views of [Pt(bpy)(ONNCH$_2$CH$_2$NNO)-ClNO$_2$]. Hydrogen atoms are small shaded circles; non-hydrogen atoms are 45% thermal ellipsoids. The "edge-on" view shows the conformation of the N,N′-dinitrosated chelate ring at the expense of obscuring some of the bipyridyl ligand's atoms, which are therefore not labeled.

Table III. Bond Distances (Å) in [Pt(bpy)(ONNCH$_2$CH$_2$NNO)ClNO$_2$]

Cl-Pt	2.357 (4)	N(1)-C(1)	1.466 (20)
N(1)-N(3)	1.278 (17)	N(1)-Pt	2.011 (12)
C(1)-C(2)	1.524 (20)	C(2)-N(2)	1.465 (19)
N(2)-N(4)	1.288 (17)	N(2)-Pt	2.008 (11)
N(3)-O(2)	1.241 (22)	N(4)-O(1)	1.255 (17)
N(11)-C(21)	1.396 (18)	N(11)-C(61)	1.300 (16)
N(11)-Pt	2.040 (9)	C(21)-C(31)	1.416 (20)
C(21)-C(22)	1.456 (17)	C(31)-C(41)	1.326 (19)
C(41)-C(51)	1.420 (23)	C(51)-C(61)	1.357 (22)
N(12)-C(22)	1.347 (17)	N(12)-C(62)	1.371 (16)
N(12)-Pt	2.072 (11)	C(22)-C(32)	1.421 (20)
C(32)-C(42)	1.352 (20)	C(42)-C(52)	1.362 (23)
C(52)-C(62)	1.399 (22)	N(5)-O(3)	1.278 (20)
N(5)-O(4)	1.130 (19)	N(5)-Pt	2.042 (15)

involves electrophilic attack by a nitrosating agent upon the deprotonated coordinated amine, as in the mechanism proposed for *sec*-amine nitrosations.[15]

Coordinated 1,2-ethanediamine is N-nitrosatable in other complexes[2,3] but always at only one nitrogen atom. In this case the bipyridyl ligand apparently acts as an electron sink, tending to increase the acidity of both amines' protons and making them both susceptible to nitrosation. Watt and Upchurch[10] in fact isolated (by deprotonation with KNH$_2$ in liquid ammonia) the purple black [Pt(bpy)(en-2H)]. They did not observe removal of two protons in other complexes.

Table IV. Bond Angles (deg) in [Pt(bpy)(ONNCH$_2$CH$_2$NNO)ClNO$_2$]

C(1)-N(1)-N(3)	117.6 (13)	C(1)-N(1)-Pt	112.5 (8)
N(3)-N(1)-Pt	127.8 (12)	N(1)-C(1)-C(2)	104.6 (12)
C(1)-C(2)-N(2)	107.6 (12)	C(2)-N(2)-N(4)	119.2 (12)
C(2)-N(2)-Pt	117.5 (8)	N(4)-N(2)-Pt	120.6 (10)
N(1)-N(3)-O(2)	118.0 (15)	N(2)-N(4)-O(1)	115.9 (14)
C(21)-N(11)-C(61)	117.8 (12)	C(21)-N(11)-Pt	114.5 (7)
C(61)-N(11)-Pt	127.5 (10)	N(11)-C(21)-C(31)	118.5 (11)
N(11)-C(21)-C(22)	115.0 (12)	C(31)-C(21)-C(22)	126.5 (13)
C(21)-C(31)-C(41)	120.6 (15)	C(31)-C(41)-C(51)	120.6 (15)
C(41)-C(51)-C(61)	115.6 (13)	N(11)-C(61)-C(51)	126.8 (15)
C(22)-N(12)-C(62)	119.4 (12)	C(22)-N(21)-Pt	114.8 (8)
C(62)-N(12)-Pt	125.7 (9)	C(21)-C(22)-N(21)	115.8 (12)
C(21)-C(22)-C(32)	123.2 (13)	N(12)-C(22)-C(32)	120.8 (11)
C(22)-C(32)-C(42)	118.9 (15)	C(32)-C(42)-C(52)	120.4 (15)
C(42)-C(52)-C(62)	120.1 (14)	N(12)-C(62)-C(52)	119.9 (14)
O(3)-N(5)-O(4)	124.8 (15)	O(3)-N(5)-Pt	114.6 (11)
O(4)-N(5)-Pt	120.6 (13)	Cl-Pt-N(1)	92.6 (4)
Cl-Pt-N(2)	89.8 (4)	N(1)-Pt-N(2)	77.8 (5)
Cl-Pt-N(11)	87.9 (3)	N(1)-Pt-N(11)	100.3 (5)
N(2)-Pt-N(11)	177.0 (5)	Cl-Pt-N(12)	89.6 (3)
N(1)-Pt-N(12)	177.9 (5)	N(2)-Pt-N(12)	102.3 (4)
N(11)-Pt-N(12)	79.7 (4)	Cl-Pt-N(5)	177.0 (4)
N(1)-Pt-N(5)	90.3 (6)	N(2)-Pt-N(5)	91.8 (5)
N(11)-Pt-N(5)	90.6 (5)	N(21)-Pt-N(5)	87.6 (5)

Table V. Anisotropic Temperature Factors[a] ($A^2 \times 10^3$) for Non-Hydrogen Atoms in [Pt(bpy)(ONNCH$_2$CH$_2$NNO)ClNO$_2$]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl	58 (2)	54 (2)	61 (2)	−9 (2)	22 (2)	−0 (2)
N(1)	55 (7)	68 (10)	52 (7)	−8 (7)	8 (6)	−1 (7)
C(1)	58 (10)	55 (10)	56 (10)	22 (9)	27 (8)	15 (8)
C(2)	61 (9)	48 (10)	56 (9)	−9 (8)	38 (7)	−11 (8)
N(2)	34 (5)	63 (9)	49 (7)	6 (6)	10 (5)	0 (6)
N(3)	88 (11)	98 (12)	58 (9)	21 (11)	27 (8)	41 (11)
N(4)	54 (8)	126 (14)	52 (8)	23 (9)	26 (6)	46 (9)
O(1)	45 (6)	163 (14)	70 (7)	17 (9)	29 (5)	33 (8)
O(2)	71 (8)	94 (10)	66 (8)	15 (8)	15 (6)	7 (8)
N(11)	21 (5)	66 (8)	47 (6)	6 (7)	6 (4)	9 (6)
C(21)	42 (8)	27 (7)	62 (9)	−8 (7)	13 (7)	−1 (6)
C(31)	52 (9)	58 (10)	53 (10)	−24 (9)	17 (7)	−1 (8)
C(41)	38 (8)	63 (11)	71 (11)	−11 (9)	11 (7)	−1 (7)
C(51)	48 (9)	53 (11)	86 (12)	−11 (9)	−14 (9)	15 (8)
C(61)	31 (7)	61 (12)	75 (11)	−2 (8)	10 (7)	9 (6)
N(12)	28 (6)	61 (8)	43 (6)	1 (6)	9 (5)	−11 (6)
C(22)	32 (7)	38 (8)	62 (10)	−6 (7)	9 (6)	9 (7)
C(32)	63 (10)	54 (10)	61 (10)	5 (8)	34 (8)	3 (8)
C(42)	55 (9)	63 (10)	58 (9)	8 (11)	14 (7)	18 (10)
C(52)	66 (11)	70 (12)	41 (9)	7 (8)	8 (8)	25 (9)
C(62)	38 (8)	70 (11)	53 (9)	4 (9)	13 (7)	−0 (8)
N(5)	48 (8)	69 (10)	72 (10)	−2 (9)	13 (7)	−21 (8)
O(3)	90 (9)	81 (9)	70 (8)	−22 (7)	40 (7)	−18 (7)
O(4)	99 (9)	57 (8)	87 (9)	−29 (7)	45 (7)	−18 (7)
Pt	37 (1)	45 (1)	42 (1)	2 (1)	14 (1)	7 (1)
Aq	100 (17)	55 (16)	90 (17)	4 (13)	56 (14)	−16 (13)

[a] The anisotropic temperature factor takes the form $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2hka^*b^*U_{12} + \ldots)$.

Table VI. Hydrogen Coordinates ($\times 10^4$) and Temperature Factors ($A^2 \times 10^3$) in [Pt(bpy)(ONNCH$_2$CH$_2$NNO)ClNO$_2$]

	x	y	z	U
H(1)C(1)	1621	−3130	1875	129 (80)
H(2)C(1)	1690	−2642	2669	143 (81)
H(1)C(2)	402	−303	2383	38 (36)
H(2)C(2)	−142	−1780	1824	76 (51)
HC(31)	5354	2790	54	82 (59)
HC(41)	6921	1382	748	21 (29)
HC(51)	6664	−508	1718	139 (76)
HC(61)	4684 (98)	−730 (177)	1976 (58)	53 (37)
HC(32)	3681	3917	−618	90 (58)
HC(42)	1912	5205	−1168	53 (41)
HC(52)	206	4290	−850	63 (43)
HC(62)	289	2290	112	58 (45)

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(11) Watt, G. W.; Upchurch, D. G. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1174.

(12) Watt, G. W.; Alexander, P. W.; Manhas, B. S. *J. Am. Chem. Soc.* **1967**, *89*, 6483.

(13) Watt, G. W.; Alexander, P. W. *Inorg. Chem.* **1968**, *7*, 537.

(14) Watt, G. W.; Hood, R. L. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3359.

(15) Fridman, A. L.; Mukhametshin, F. M.; Novikov, S. S. *Russ. Chem. Rev.* **1971**, *40*, 1.

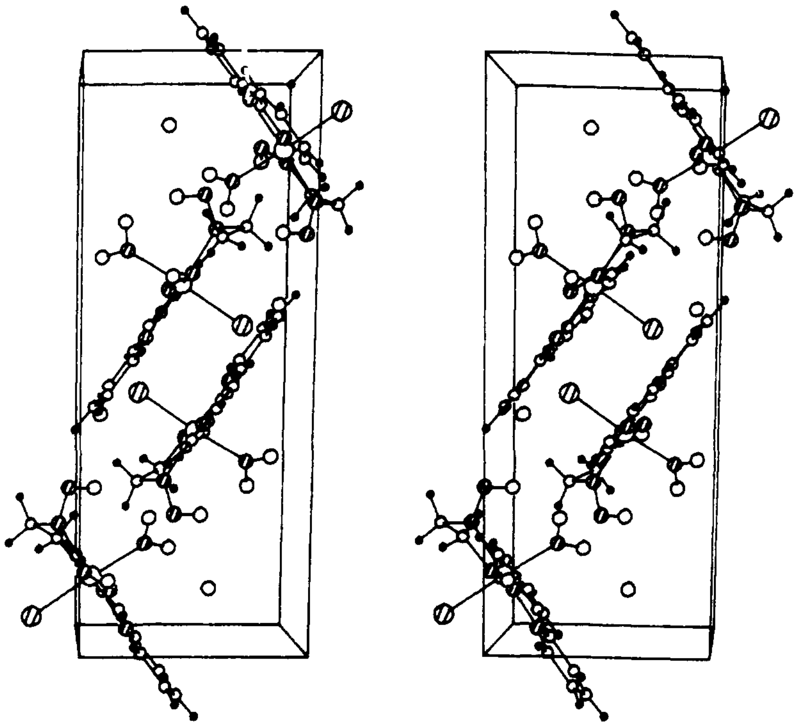

Figure 2. Stereographic view of the packing in crystal of [Pt(bpy)($ONNCH_2CH_2NNO$)$ClNO_2$]. Pt, O, and C atoms are represented by large, medium, and small open circles. Cl and N atoms are represented by larger and smaller hatched circles. Hydrogens are small filled circles.

Two views of the molecular structure of [Pt(bpy)($ONNCH_2CH_2NNO$)$ClNO_2$] are given in Figure 1. Figure 2 is a stereoscopic view of the crystal packing. Atomic coordinates are given in Tables II and VI. Tables III–V summarize bond distances, angles, and atom temperature factors.

As might be expected, N,N′-dinitrosation flattens and distorts the Pt–en chelate ring substantially. The substituents at the amine N's are now more nearly trigonally than tetrahedrally arranged. The torsion angle N(1)–C(1)–C(2)–N(2) is only 39.6 (1.5)°. The comparable angle in unsubstituted Pt–en rings is larger, 54.6 (8)°,[16] 53.55°,[17] or even 68°.[18] The bite angle, N(1)–Pt–N(2), at 77.8 (5)°, is also significantly less than in comparison Pt–en rings. Moreover, both C(1) and C(2) lie on the same side of the Pt–N(1)–N(2) plane, the chloride side, (see Figure 1b).

A comparison of the two *N*-nitroso groups' bond angles and distances shows that they have essentially the same internal geometries (see Tables III and IV). They are, however, quite differently disposed with respect to the rest of the molecule. The first, N(1)–N(3)–O(2), is anti to the carbons of the adjoining chelate ring, and the second (N(2)–N(4)–O(1)) is syn. Neither N–N–O group lies particularly near the Pt–N(1)–N(2) plane, but the anti *N*-nitroso extends much farther away than the syn. O(2) lies 1.553 Å away from this plane on the nitrite side and O(1) lies only 0.625 Å away. Furthermore, the five atoms in the two Pt(C)NNO moieties are close to but not coplanar. The Pt and C(1) deviate −0.267 and −0.165 Å from the anti nitroso (N(1)–N(3)–O(2)) plane, and the Pt and C(2) deviate 0.297 and 0.204 Å from the syn nitroso (N(2)–N(4)–O(1)) plane. The anti nitroso O (O(2)) lies close to the bipyridyl carbon atom C(61) (d = 2.956 Å) and to the nitro oxygen O(3) (d = 2.943 Å). It is hydrogen bonded to the half-occupancy water of crystallization (d = 2.687 Å). For its part, the water of crystallization lies 2.878 Å from O(4) of another molecule (Figure 2). These hydrogen bonds hold the structure together. Meanwhile the closest intermolecular approach for O(1) is 3.188 Å to C(41) of the neighboring molecule at $(1 + x, y, z)$.

The geometry of the nitro group reflects the effects of the approach of the anti nitroso O. One N to O bond distance, N(5)–O(3) (1.278 (20) Å), is strikingly greater than the other (N(5)–O(4) (d = 1.130 (19) Å). The longer of these two exceeds all except one of the N–O distances in N-coordinated nitro groups summarized in a recent review;[19] the shorter is less than any comparable distance in the same summary, again with one exception.

Strong acid catalyzes the denitrosation of ordinary *N*-nitrosamines.[15] In hot concentrated HCl the complex [Pt(bpy)($ONNCH_2CH_2NNO$)$ClNO_2$] loses two nitrogen atoms per platinum and therefore also is (at least half) denitrosated under these conditions. The denitrosation product analyzes for [Pt(bpy)($NH_2CH_2CH_2NNO$)Cl_2]$Cl\cdot 2H_2O$ or [Pt(bpy)(en)$ClNO_2$]$Cl_2\cdot H_2O$. Comparison of the infrared spectra of the precursor [Pt(bpy)(en)Cl_2]$Cl_2\cdot 5H_2O$, the dinitrosated complex, and this product shows that new absorptions appear at 828, 850, 1260, 1315, 1360, and 1490 cm^{-1} upon conversion to the dinitrosated chloronitro complex and that of these only the ones at 828, 1260, and 1315 cm^{-1} persist after the HCl treatment. This suggests the loss of the nitro group and retention of one *N*-nitroso function rather than complete denitrosation because absorptions associated with N-coordinated NO_2 are lost—in $K_2Pt(NO_2)_4Br_2$[19] the nitro ligands absorb at 842, 1328, 1460, and 1475 cm^{-1}.

In *N*-nitrosamines there is a considerable barrier to rotation about the N–N bond. In $(CH_3)_2NNO$, for instance, $\Delta G^\ddagger$ for rotation is 96.2 kJ/mol.[20] Values in other *N*-nitrosamines are similar. The N–N bond distance is 1.344 Å in $(CH_3)_2NNO$.[21] The hindrance to rotation about N–N is ascribed to partial double bond character. The ground-state electronic configuration of *N*-nitrosamines has been assessed by SCF calculations to possess 48% of the 1,3 dipolar character:[22] $(R)_2N^+{=}N{-}O^-$. In [Pt(bpy)($ONNCH_2CH_2NNO$)$ClNO_2$] both N–N bonds are significantly shorter than 1.344 Å. They average 1.283 Å (Table

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(16) Freeman, W. A. *Inorg. Chem.* **1976**, *15*, 2235–2239.

(17) Liu, C. F.; Ibers, J. *Inorg. Chem.* **1970**, *9*, 773–778.

(18) Iball, J.; MacDonald, M.; Scrimgeour, S. *Acta Crystallogr., Sect. B.* **1975**, *B31*, 1672.

(19) Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55–132.

(20) Cooney, J. D.; Brownstein, S. K.; ApSimon, J. W. *Can. J. Chem.* **1974**, *52*, 3028–3036.

(21) Rademacher, P.; Stolevik, R. *Acta Chem. Scand.* **1969**, *23*, 672.

(22) Tanaka, J. *J. Chem. Soc. Jpn.* **1957**, *78*, 1647.

Table VII. Carbon NMR Chemical Shifts[a] for Three Pt Complex Ions

C_2[b]	C_6	C_4	C_5	C_3	en
$[Pt(bpy)(en)]^{2+}$ (in D_2O Solution)[c]					
156.93	151.62	142.97	129.52	125.19	48.33
trans-$[Pt(bpy)(en)Cl_2]^{2+}$ (in D_2O Solution)					
155.05	151.30	145.79	131.78	128.09	49.08
$[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ (in DMF Solution)					
154.12	150.35	143.35	128.24	125.62	54.62
153.62	149.85	143.02	127.45	124.98	49.89

[a] Chemical shifts in ppm vs. external Me_4Si; measured vs. external Me_4Si or vs. internal DMF. [b] Bipyridyl carbons are conventionally numbered. [c] From ref 24.

II). This means there is even more double bond character in the N–N bonds in the complex nitrosamine than in ordinary nitrosamines and consequently a larger barrier to rotation. By use of the equations developed by Gouesnard and Martin,[23] $\Delta G^{\ddagger}$ for rotation about a 1.283-Å N–N bond can be estimated at 143 kJ/mol, which would mean the effective elimination of such rotations in this complex.

In the crystal one of the bent NNO groups is syn to the five-membered ring's carbons, and the other is anti (Figure 1). From this fact and the large barrier to N–N rotation, it follows, on steric grounds, that the five-membered chelate ring cannot in solution undergo rapid conformational inversion. The process would require the anti NNO to rotate out of the way as it passed the plane of the bipyridyl. The ^{13}C NMR spectrum of $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ is not inconsistent with this conclusion. Every carbon atom in the molecule has a different chemical shift. Table VII shows the ^{13}C δ values in comparison to those of the molecule's two unnitrosated precursors. The bipyridyl ligand resonance assignments follow those of Erickson, Sarneski, and Reilley.[24]

It has been found[20,25] that a given α-carbon resonates at higher field when syn to a nitrosamino than when anti to the same group. The syn–anti differences are in the range of 5–7 ppm. In $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ one of the two en carbon atoms is substantially deshielded upon N,N′-dinitrosation and the other resonates at nearly the same field as before N-nitrosation (Table VII). The deshielded resonance therefore probably comes from the methylene carbon anti to its neighboring nitroso O, that is, C(1).

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Registry No. $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]\cdot 0.5H_2O$, 85116-30-9; $[Pt(bpy)(en)Cl_2]Cl_2$, 85116-31-0.

Supplementary Material Available: A listing of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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[23] Gouesnard, J. P.; Martin, G. J. *Org. Magn. Reson.* **1979**, *12*, 263–270.

[24] Erickson, L. E.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1975**, *14*, 3007–3017.

[25] Chow, Y. L.; Polo, J. *Org. Magn. Reson.* **1981**, *15*, 201.

Trefoil Aromatics: A Potentially New Class of Aromatic Molecules

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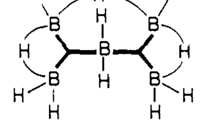
Abstract: A potentially new class of aromatic molecules termed *trefoil aromatics* is postulated. The system possesses a three-center, two-electron bond (trefoil bond) that is imbedded in the center of an annulene perimeter containing $4n + 2$ π electrons. In a sense, the trefoil bond takes the place of an atom. The concept is generalized to include variations of annulene perimeters and heteroatom incorporation. Also considered are the trefoil cations that result from the center protonation of the trefoil bond. The postulated stability of prototype species is evaluated relative to their valence isomers by molecular orbital calculations.

It is well-known that physicochemical properties of annulenes can be modified significantly by intramolecular union(s) and by enclosing another π system inside the perimeter.[1-3] Recently, annulene perimeters have been considered as a potential host to stabilize novel substructures such as a planar tetracoordinate carbon atom.[4] In this paper we wish to examine a potentially new class of aromatic molecules, *trefoil aromatics*, that incorporates a three-center, two-electron bond within an annulene perimeter containing $4n + 2$ π-electrons.

The three-center, two-electron bonding of interest is now well established and occurs in pentaborane (B_5H_{11}) and higher homologues.[5] One representation of the B_5H_{11} molecule considers the apical BH_2 group to be bound to the remaining four borons in pairs through three-center bonds of the type shown schematically in heavy lines (I). Although there is no really adequate valence-bond description of pentaborane, a molecular orbital



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[1] Heilbronner, H.; Bock, H. "Das HMO-Modell und Seine Anwendung"; Verlag Chemie: Weinheim/Bergstl., Germany, 1968.

[2] Hellwinkel, D. *Chem.-Ztg.* **1970**, *94*, 715.

[3] The perimeter model[1] to analyze the orbital interactions between an annulene perimeter and an enclosed π system is useful in predicting the stability of condensed cyclic π-electron systems (Fukunaga, T. Third International Symposium on Novel Aromatic Compounds, San Francisco, Aug 1977).

[4] Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181. Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. R. *Tetrahedron* **1981**, *37*, 921 and references therein.

[5] "Boron Hydride Chemistry"; Muetterties, E. L., Ed., Academic Press: New York, 1975: Muetterties, E. L., Chapter 1, Lipscomb, W. N., Chapter 2.

0002-7863/83/1505-2729$01.50/0