antisymmetric coupling within the copper(II) pairs. In principle, they could lead to a zero resulting magnetic moment as well. This canceling effect is schematized as

Right now, we do not see well the conditions which have to be fulfilled to favor one situation rather than another. We hope to be able to clarify this question in the near future.

As a conclusion, we want to point out that weak ferromagnetism in molecular chemistry deserves to be investigated in a thorough fashion. It might be also an interesting strategy to design molecular-based materials exhibiting a zero-field magnetization. This paper is one of the first ones focusing on this facet of molecular magnetism.

It is also worth emphasizing that, in most of the copper(II) terephthalate derivatives, the metal ions are magnetically isolated or very weakly coupled.[45,46] In one or two cases, owing to quite favorable orientations of the magnetic orbitals, a rather large antiferromagnetic interaction is detected.[33,47] In **2**, the terephthalate groups propagate a ferromagnetic interaction between residual pair magnetic moments. Another case of ferromagnetism in copper(II) terephthalate derivatives has been recently reported.[48]

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Supplementary Material Available: Tables of crystal data collection parameters and refinement conditions, anisotropic temperature factors, important least-squares planes, and hydrogen coordinates (5 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

(45) Verdaguer, M.; Gouteron, J.; Jeannin, S.; Jeannin, Y.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 4291.
(46) Bakalbassis, E. G.; Mrozinski, J.; Tsipis, C. A. *Inorg. Chem.* **1986**, *25*, 3684.
(47) Bakalbassis, E. G.; Tsipis, C. A.; Mrozinski, J. *Inorg. Chem.* **1985**, *24*, 4291.
(48) Bakalbassis, E. G.; Kahn, O.; Bergerat, P.; Jeannin, S.; Jeannin, Y.; Dromzee, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1771.

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Platinum(IV) Complexes of a Tetraaza Macrocycle with Pendent Dichloroamine or Ammonium Groups

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Reaction of the platinum(II) complex of the pendent-arm macrocycle 6,13-diammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane with chlorine in aqueous solution does not lead simply to oxidation of the platinum(II) complex to a *trans*-dichloroplatinum(IV) complex. Instead, complete chlorination of the pendent primary amines occurs also, producing the *trans*-dichloroplatinum(IV) complex of a bis(dichloroamino) macrocycle. The dichloroamino complex was characterized by a crystal structure analysis, the first X-ray crystal structure of a dichloroamine; the perchlorate salt of *trans*-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$ crystallized in the $P2_1/n$ space group, with $Z = 2$, $a = 10.612$ (5) Å, $b = 10.280$ (3) Å, $c = 12.792$ (4) Å, and $\beta = 110.56$ (3)°. Inequivalent N–Cl bond lengths (1.718 (12) and 1.779 (12) Å) were observed. In aqueous acid, slow dechlorination occurs to produce the *trans*-dichloroplatinum(IV) complex of the precursor macrocycle, also characterized by a crystal structure analysis. The complex of the precursor macrocycle, *trans*-$[Pt(\mathbf{1})Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$, crystallized in the $P\bar{1}$ space group, with $Z = 1$, $a = 7.308$ (2) Å, $b = 10.448$ (2) Å, $c = 10.672$ (2) Å, $\alpha = 103.89$ (1)°, $\beta = 104.50$ (1)°, and $\gamma = 103.90$ (1)°.

Although the syntheses and reactivities of chloroamine compounds have been well studied and reviewed,[2-4] structural studies of these compounds have been few. This paucity stems from the inherent instability of these compounds; in fact, many are explosive. An earlier paper[5] reported the syntheses and X-ray crystal structures of square-planar platinum(II) and palladium(II) complexes of the pendent-arm macrocycle 6,13-diammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane (**1**). The platinum(II) complex of this macrocycle was reacted with chlorine in order to investigate the competition between the oxidant and the pendent primary amines for the axial coordination sites on going from square-planar (Pt^{II}) to octahedral (Pt^{IV}) geometry. The product was found to be a *trans*-dichloro(tetraamine)platinum(IV) complex, but chlorination of both pendent amines also occurred, resulting in the novel coordinated macrocycle (6,13-bis(dichloroamino)-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane) (**2**). The X-ray crystal structures of the complex *trans*-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$ and the analogue *trans*-$[Pt(\mathbf{1})Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$, resulting from chloroamine hydrolysis, are reported herein. The former is, we believe, the first X-ray crystal structure of a dichloroamine compound.

Experimental Section

Syntheses. The *trans*-(6-ammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecan-13-amine)platinum(II) perchlorate complex, *trans*-$[Pt(\mathbf{1}\text{-}H)](ClO_4)_3$, was prepared as described previously.[5]

***trans*-Dichloro(6,13-bis(dichloroamino)-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)platinum(IV) Perchlorate, *trans*-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$.** *Caution!* Complexes isolated in this synthesis are slightly shock sensitive and represent an explosive hazard. In a well-ventilated fume hood, a stream of chlorine gas was bubbled through a solution of *trans*-$[Pt(\mathbf{1}\text{-}H)](ClO_4)_3$ in water (500 mL). The solution became immediately cloudy, and the chlorine supply was maintained for 15 min. Following this, the solution was purged with nitrogen for 15 min to remove excess chlorine. An unstable, off-white precipitate was removed by filtration and carefully discarded. The filtrate was concentrated on a rotary evaporator to ca. 100 mL and acidified with perchloric acid (3 mL, 5 M). Precipitation of the product as colorless plates occurred within 1 day, and these were collected, washed with ethanol and diethyl ether, and dried in a vacuum desiccator. The yield was quantitative. Crystals of satisfactory quality for X-ray work were grown by slow evaporation of a solution of the complex in acetonitrile/water (9:1). Anal. Calcd for $C_{12}H_{26}Cl_8N_6O_8Pt$: C, 16.7; H, 3.0; N, 9.7. Found: C, 17.1; H, 3.2; N, 9.8. Electronic spectrum [water; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 294 (780),

(1) (a) University of Newcastle. (b) University of Sydney.
(2) Drago, R. S. *J. Chem. Educ.* **1957**, *34*, 541.
(3) Schmitz, E. *Angew. Chem.* **1961**, *73*, 23.
(4) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639.
(5) Bernhardt, P. V.; Lawrance, G. A.; Curtis, N. F.; Siriwardena, A.; Patalinghug, W. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1990**, 2853.

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Table I. Crystallographic Data for the Platinum(IV) Complexes

	trans-$[Pt(2)Cl_2](ClO_4)_2$	*trans*-$[Pt(1)Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$
space group	$P2_1/n$	$P\bar{1}$
a, Å	10.612 (5)	7.308 (2)
b, Å	10.280 (3)	10.448 (2)
c, Å	12.792 (4)	10.672 (2)
α, deg		103.89 (1)
β, deg	110.56 (3)	104.50 (1)
γ, deg		103.90 (1)
V, Å^3	1307.2	726.7
fw	861.1	868.3
ρ_{calcd}, g cm^{-3}	2.187	1.987
empirical formula	$C_{12}H_{26}Cl_8N_6O_8Pt$	$C_{12}H_{40}Cl_6N_6O_{12}Pt$
Z	2	1
$F(000)$	836	430
abs coeff, cm^{-1}	62.15	54.4
transm coeff	0.51–0.86	0.146–0.277
temp, °C	21	21
λ, Å	0.710 69	0.710 69
$R(F_o)$, $R_w(F_o)$[a]	0.041, 0.043	0.019, 0.020

[a] $R(F_o) = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w(F_o) = \sum(||F_o| - |F_c||)w^{1/2}/\sum|F_o|w^{1/2}$.

201 (6400). ^{1}H NMR (CD_3CN; δ): 1.48, s (6 H); 3.24, m (8 H); 3.44, s (8 H). ^{13}C NMR (CD_3CN; δ): 17.2, 55.6, 56.7, 63.2.

***trans*-Dichloro(6,13-diammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)platinum(IV) Chloride Perchlorate Tetrahydrate, *trans*-$[Pt(1)Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$.** This was prepared in the same manner as *trans*-$[Pt(2)Cl_2](ClO_4)_2$, except hydrochloric acid (2 mL, 3 M), instead of perchloric acid, was added to the filtered and concentrated reaction mixture. Colorless crystals of X-ray quality formed after ca. 14 days and these were collected, washed with ethanol, and air-dried. Anal. Calcd for $C_{12}H_{40}Cl_6N_6O_{12}Pt$: C, 16.6; H, 4.65; N, 9.7. Found: C, 16.8; H, 4.7; N, 9.8. Electronic spectrum [water; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 330 (160), 267 (1030), 209 (265 000). ^{1}H NMR (D_2O; δ): 1.67, s (6 H); 2.88, 3.66, q (8 H); 3.33, s (8 H). ^{13}C NMR (D_2O; δ): 18.0, 53.8, 54.6, 61.1.

Crystallography. Cell constants were determined by a least-squares fit to the θ values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. The crystallographic data for *trans*-$[Pt(2)Cl_2](ClO_4)_2$ and *trans*-$[Pt(1)Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$ are summarized in Table I. Data were reduced and Lorentz, polarization, and decomposition corrections were applied using the Enraf-Nonius Structure Determination Package. The structures were solved by Patterson methods and refined by full-matrix least-squares analysis with SHELX-76.[6] Absorption was by numerical methods using a Gaussian grid. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined (for *trans*-$[Pt(1)Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$) or included at calculated sites (C–H = 0.97 Å) with group isotropic thermal parameters. Scattering factors and anomalous dispersion corrections used for Pt were taken from ref 7, and all others were those supplied in SHELX-76. Non-hydrogen atom coordinates are listed in Table II. The atomic nomenclature is defined in Figure 1.[8]

Results and Discussion

The platinum(IV) complex cation *trans*-$[Pt(2)Cl_2]^{2+}$ was synthesized by bubbling chlorine through an aqueous solution of the platinum(II) complex of **1** at room temperature for 15 min. Filtration and concentration of the reaction mixture, followed by addition of dilute perchloric acid, resulted in precipitation of the sparingly soluble *trans*-$[Pt(2)Cl_2](ClO_4)_2$ within 1 day. Crystals of satisfactory quality for X-ray analysis were grown by slow evaporation of a solution of *trans*-$[Pt(2)Cl_2](ClO_4)_2$ in acetonitrile/water (9:1). The dechlorinated platinum(IV) complex *trans*-$[Pt(1)Cl_2]^{4+}$ was prepared similarly to *trans*-$[Pt(2)Cl_2]^{2+}$, although precipitation of *trans*-$[Pt(2)Cl_2]^{2+}$ as the perchlorate salt was avoided by the addition of dilute hydrochloric acid instead of perchloric acid. Evaporation of the reaction mixture over a period of ca. 2 weeks afforded crystals of *trans*-$[Pt(1)Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$. It appears that the synthesis of *trans*-$[Pt(1)Cl_2]^{2+}$ proceeds via the intermediate *trans*-$[Pt(2)Cl_2]^{2+}$, which dechlorinates slowly in aqueous acid if precipitation is avoided (Scheme I).

The electronic spectrum of *trans*-$[Pt(2)Cl_2]^{2+}$ exhibited a maximum at 294 nm (ϵ 780 M^{-1} cm^{-1}). The absorbance is due

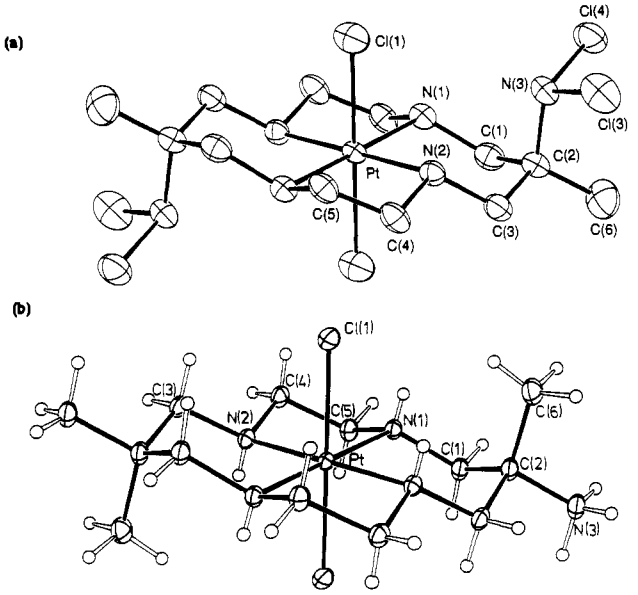


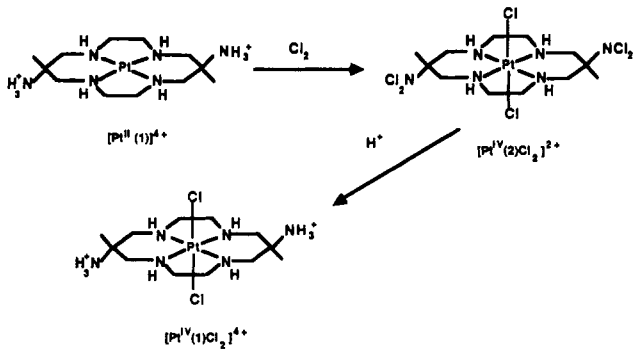
Figure 1. ORTEP drawing of the complex cations (a) *trans*-$[Pt(2)Cl_2](ClO_4)_2$ and (b) *trans*-$[Pt(1)Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$.

Table II. Non-Hydrogen Positional Parameters ($\times 10^4$) for *trans*-$[Pt(2)Cl_2](ClO_4)_2$ and *trans*-$[Pt(1)Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$

	x	y	z
	trans-$[Pt(2)Cl_2](ClO_4)_2$		
Pt(1)	5000	5000	5000
Cl(1)	3544 (4)	6688 (5)	4335 (4)
N(1)	6197 (10)	6035 (10)	6341 (8)
N(2)	3819 (10)	4210 (11)	5808 (8)
N(3)	5521 (12)	4674 (10)	8048 (10)
C(1)	5469 (14)	6642 (13)	7010 (11)
C(2)	4607 (12)	5768 (13)	7472 (10)
C(3)	3429 (12)	5138 (15)	6538 (10)
C(4)	2635 (13)	3622 (14)	4898 (11)
C(5)	3112 (15)	2994 (13)	4097 (11)
C(6)	4097 (18)	6525 (16)	8227 (13)
Cl(2)	5283 (5)	−347 (4)	2962 (5)
O(21)	5481 (22)	−312 (20)	1872 (18)
O(22)	6138 (19)	569 (17)	3582 (19)
O(23)	3924 (14)	−73 (15)	2706 (15)
O(24)	5693 (19)	−1548 (14)	3397 (13)
Cl(3)	4630 (6)	3610 (6)	8639 (4)
Cl(4)	6859 (4)	5195 (5)	9178 (3)
	trans-$[Pt(1)Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$		
Pt	0	0	0
Cl(1)	2255 (1)	9739 (1)	8856 (1)
N(1)	165 (3)	8226 (2)	10473 (2)
N(2)	2239 (3)	11010 (2)	11845 (2)
N(3)	−4695 (3)	5440 (2)	8285 (2)
C(1)	−1762 (3)	7100 (2)	10057 (2)
C(2)	−2912 (3)	6650 (2)	8516 (2)
C(3)	3797 (3)	12255 (2)	11902 (2)
C(4)	3071 (3)	9937 (2)	12255 (2)
C(5)	1298 (3)	8666 (2)	11967 (2)
C(6)	−1739 (4)	6137 (3)	7614 (3)
Cl(2)	3012 (1)	1778 (1)	5701 (1)
O(21)	2437 (4)	2403 (3)	6825 (2)
O(22)	1520 (5)	1631 (4)	4450 (3)
O(23)	3139 (7)	440 (4)	5656 (4)
O(24)	4892 (6)	2657 (5)	5796 (5)
Cl(3)	3029 (1)	6497 (1)	160 (1)
O(1)	2226 (5)	5043 (3)	5986 (4)
O(2)	1714 (5)	7260 (3)	5121 (5)

(6) Sheldrick, G. M. SHELX-76: A Program for X-Ray Crystal Structure Determination. University of Cambridge, England, 1976.
(7) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(8) Figures were drawn with ORTEP (Johnson, C. K. *ORTEP, A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965).

Scheme I



predominantly to the presence of the dichloroamine groups. The electronic spectrum of *N,N*-dichloromethylamine exhibits a maximum at 303 nm (ϵ 260),[9] which is comparable in energy and intensity to that found in the spectrum of *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$, remembering that the two dichloroamine groups in the complex should result in a doubling in intensity relative to CH_3NCl_2. This assignment was confirmed by the spectrum of *trans*-$[Pt(\mathbf{1})Cl_2]^{4+}$, which displayed maxima of lower intensity at 330 (ϵ 160) and 267 nm (ϵ 1030). By contrast to the spectrum of *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$, these transitions are purely of d–d origin, and the energies and intensities of these maxima are comparable with those reported for the spectrum of *trans*-$[Pt(en)_2Cl_2]^{2+}$ [332 (ϵ 105) and 263 nm (ϵ 950)],[10] where both transitions are derived from the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition split by the axially symmetric ligand field. Evidently, the anticipated d–d maxima in the spectrum of *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ have been obscured by the more intense chloroamine transition. The N–Cl stretching vibration was identified in the infrared spectrum at 730 cm^{-1} and is comparable in energy with those of other studies.[11] The spectrum of *trans*-$[Pt(\mathbf{1})Cl_2]^{4+}$, in contrast to that of the chloroamine precursor, displayed broad resonances at 1615 and 1500 cm^{-1}, characteristic of a primary ammonium group [δ(H–N–H)]. The proton-decoupled ^{13}C NMR spectrum of *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ in acetonitrile exhibits only four resonances, consistent with the high symmetry of the molecule. The pendent methyl resonance at 17.2 ppm is shifted only slightly from the position found in the spectrum of the platinum(II) precursor or *trans*-$[Pt(\mathbf{1})Cl_2]^{4+}$ (near 18.0 ppm), indicative of no chemistry at the pendent methyl group and only reaction at the pendent amines, as anticipated.

The structure determination of *trans*-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$ found the complex cation to be located on a center of symmetry with a pair of perchlorate anions situated on inversion-related general sites. A drawing of the complex cation appears in Figure 1a, where hydrogen atoms have been deleted for clarity; selected bond distances and angles appear in Table III. Coordination of chloro ligands in the axial sites of the complex is apparent, with the macrocycle adopting the same geometry as found in the platinum(II) precursor.[5] The geometry of the pendent dichloroamine groups is trigonal pyramidal, with inequivalent N–Cl bond lengths of 1.718 (12) and 1.779 (12) Å, a Cl–N–Cl angle of 103.9 (6)°, and Cl–N–C angles of 112.4 (9) and 108.7 (9)°. We believe this is the first X-ray crystal structure of an organic dichloroamine. The only closely comparable structure is that of *N,N*-dichloromethylamine, which was determined by electron diffraction,[12] where the N–Cl bond lengths were found to be 1.74 (2) Å and the Cl–N–Cl angle was 108 (1)°. It is interesting that the pendent dichloroamine groups were not protonated even though the complex was isolated initially from acidic solution. The presence of the two chloro groups evidently diminishes the basicity of the amine relative to a primary amine. Nevertheless, there has been

Table III. Selected Bond Lengths and Angles for the Complex Cations in *trans*-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$ and *trans*-$[Pt(\mathbf{1})Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$

Bond Lengths (Å)

	trans-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$	*trans*-$[Pt(\mathbf{1})Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$
Pt–Cl(1)	2.280 (5)	2.312 (1)
Pt–N(1)	2.040 (10)	2.057 (2)
Pt–N(2)	2.052 (10)	2.057 (2)
N(1)–C(1)	1.477 (16)	1.485 (3)
N(1)–C(5)	1.490 (15)	1.498 (3)
N(2)–C(3)	1.492 (16)	1.486 (3)
N(2)–C(4)	1.507 (14)	1.499 (3)
N(3)–C(2)	1.499 (16)	1.502 (3)
N(3)–Cl(3)	1.779 (12)	
N(3)–Cl(4)	1.718 (12)	
C(1)–C(2)	1.542 (17)	1.543 (3)
C(2)–C(3)	1.536 (17)	1.543 (3)
C(2)–C(6)	1.483 (17)	1.528 (3)
C(4)–C(5)	1.445 (19)	1.522 (3)

Bond Angles (deg)

	trans-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$	*trans*-$[Pt(\mathbf{1})Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$
N(1)–Pt–Cl(1)	93.3 (3)	88.2 (1)
N(2)–Pt–Cl(1)	92.0 (3)	92.2 (1)
N(2)–Pt–N(1)	95.3 (4)	84.4 (1)
Cl(1)–Pt–Cl(1)	180.0	180.0
C(1)–N(1)–Pt	114.2 (8)	115.8 (1)
C(3)–N(2)–Pt	114.5 (8)	116.0 (1)
C(4)–N(2)–Pt	106.1 (8)	107.0 (1)
Cl(3)–N(3)–C(2)	108.7 (9)	
Cl(4)–N(3)–C(2)	112.4 (9)	
Cl(4)–N(3)–Cl(3)	103.9 (6)	

a report of the structure of the *N*-chloro-*N,N*-diethylammonium cation, crystallized as the hexachloroantimonate(V) salt, where the amine was indeed protonated.[13] In that structure the N–Cl bond lengths in the two crystallographically independent cations were found to be 1.756 (13) and 1.784 (14) Å. A low-temperature X-ray crystal structure of NCl_3 has also been reported, wherein distances [N–Cl = 1.75 (1) Å] and angles [Cl–N–Cl = 106.8 (2)°][14] again approximate those reported here.

The X-ray crystal structure determination of the centrosymmetric complex cation *trans*-$[Pt(\mathbf{1})Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$ defined a coordination sphere similar to that found in *trans*-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$, and a drawing of the molecule appears in Figure 1b. The dichloroamine groups in *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ have clearly undergone dechlorination, yielding pendent ammonium groups. The Pt–N bond lengths in *trans*-$[Pt(\mathbf{1})Cl_2]^{4+}$ [2.057 (2) Å] are not significantly different from those found in the structure of the chloroamine analogue [2.04 (1) and 2.05 (1) Å], but the better quality of data for the former structure allowed a more precise coordination sphere geometry to be defined. The Pt–Cl bond lengths are somewhat different in the two structures [2.280 (5) Å in *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ and 2.312 (1) Å in *trans*-$[Pt(\mathbf{1})Cl_2]^{4+}$], but the origins of this discrepancy are not clear. A somewhat surprising observation was that all four secondary amine nitrogens in *trans*-$[Pt(\mathbf{1})Cl_2]^{4+}$ had inverted, relative to their positions in the precursors $[Pt(\mathbf{1})]^{4+}$ and *trans*-$[Pt(\mathbf{2})Cl_2]^{4+}$. The dispositions of the pendent groups in the present case resemble those found in the palladium(II) analogue of $[Pt(\mathbf{1})]^{4+}$.[5] It is quite uncommon for inert complexes to undergo inversion at their coordinated secondary amines in acidic solution. The pK_a values of these coordinated amines are generally high, although the pK_a values of amine complexes of tetravalent metal ions such as vanadium(IV)[15] and platinum(IV)[16] may be quite low, and often full pro-

(9) Haag, W. R. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1123.
(10) Basolo, F.; Bailar, J. C., Jr.; Rapp Tarr, B. *J. Am. Chem. Soc.* **1950**, *72*, 2433.
(11) Heasley, V. L.; Kovacic, P.; Lange, R. M. *J. Organomet. Chem.* **1966**, *31*, 3050.
(12) Stevenson, D. P.; Schomaker, V. *J. Am. Chem. Soc.* **1940**, *62*, 1913.
(13) Theil, N.; Schwarz, W.; Schmidt, A. *Z. Naturforsch.* **1981**, *36B*, 775.
(14) Von Hartl, H.; Schoner, J.; Jander, J.; Schulz, H. *Z. Anorg. Allg. Chem.* **1975**, *413*, 61.
(15) Comba, P.; Engelhardt, L. M.; Harrowfield, J. M.; Lawrance, G. A.; Martin, L. L.; Sargeson, A. M.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 174.

tonation of the complex is only achieved in strong acid. Remembering that inversion must have taken place during the dechlorination process (acidic solution), and not during the initial chlorination (neutral solution), it is clear that the pK_a values of the present platinum(IV) complexes are also quite low.

The complex *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ was found to be quite stable in acetonitrile, since the crystal used in the X-ray structure was grown over a period of several weeks. However, it was found that the pendent chloroamine groups slowly dechlorinated in acid, resulting in the complex *trans*-$[Pt(\mathbf{1})Cl_2]^{4+}$. Recall that the chloroamine complex was stable in aqueous solution for at least 1 day before it precipitated as the perchlorate salt, so although the decomposition is not rapid, dechlorination of both pendent amines does occur over a period of a couple of weeks in acidic solution. Rapid precipitation of *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ was avoided by acidificiation of the reaction mixture with hydrochloric acid instead of perchloric acid, and it was apparent that the chloride salt of *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ was sufficiently soluble that precipitation did not occur before dechlorination. Acid-catalyzed dechlorination of chloroamines is well-known,[17] and the observed reaction of *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ is in accord with this. Despite the observed acid-catalyzed decomposition of *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$, the stability of the complex was still remarkable by comparison with most chloroamine compounds. An extensive pyrolytic study[18] revealed that chloroamines possessing α-hydrogen atoms generally decompose by elimination of HCl to generate either a chloroimine or a nitrile depending on the whether one or two molecules of HCl are eliminated, respectively. It has been found that the presence of a tertiary carbon adjacent to the chloroamine group acts to stabilize the compound. For example, *N,N*-dichloro-*tert*-butylamine may be safely distilled without noticeable decomposition.[19] The pendent methyl groups in *trans*-$[Pt(\mathbf{2})Cl_2]^{2+}$ evidently act to stabilize the dichloroamine groups in a similar manner.

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Registry No. **1**, 138383-04-7; *trans*-$[Pt(\mathbf{1}\text{-H})](ClO_4)_3$, 131076-94-3; *trans*-$[Pt(\mathbf{1})Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$, 138333-51-4; *trans*-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$, 138353-16-9.

Supplementary Material Available: Tables of complete crystal data, thermal parameters, and derived hydrogen positional and thermal parameters for *trans*-$[Pt(\mathbf{1})Cl_2]Cl_2(ClO_4)_2 \cdot 4H_2O$ and *trans*-$[Pt(\mathbf{2})Cl_2](ClO_4)_2$ (4 pages); listings of structure factors for the same compounds (34 pages). Ordering information is given on any current masthead page.

(16) Boucher, H. A.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 4652.
(17) Field, K. W.; Kovacic, P.; Herskovitz, T. *J. Org. Chem.* **1970**, *35*, 2146.
(18) Roberts, J. T.; Rittberg, B. R.; Kovacic, P. *J. Org. Chem.* **1981**, *46*, 4111.
(19) Zimmer, H.; Audrieth, L. F. *J. Am. Chem. Soc.* **1954**, *76*, 3856.

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Activation of the Trans Geometry in Platinum Antitumor Complexes. Synthesis, Characterization, and Biological Activity of Complexes with the Planar Ligands Pyridine, *N*-Methylimidazole, Thiazole, and Quinoline. Crystal and Molecular Structure of *trans*-Dichlorobis(thiazole)platinum(II)

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The presence of planar ligands in *trans*-$[PtCl_2(py)_2]$ (py = pyridine) greatly enhances the cytotoxicity of such species, with respect both to their corresponding cis isomer and also to *trans*-$[PtCl_2(NH_3)_2]$. The cytotoxicity of *trans*-$[PtCl_2(py)_2]$ in murine tumor cell lines is equivalent to the anticancer drug cisplatin, *cis*-$[PtCl_2(NH_3)_2]$ (*J. Med. Chem.* **1989**, *32*, 2240). The generality of this effect has been studied for a range of structures with planar ligands of formula *trans*-$[PtCl_2(L)(L')]$. Three distinct series have been examined—(i) L = L' = pyridine (py), *N*-methylimidazole (*N*-MeIm), and thiazole (Tz), (ii) L = quinoline (quin) and L' = substituted sulfoxide R'R''SO, where R' = Me and R'' = Me, CH_2Ph, and Ph, and (iii) L = quinoline and L' = NH_3. The synthesis and chemical characterization of all new complexes are described. An X-ray crystal structure determination for *trans*-$[PtCl_2(Tz)_2]$ confirmed the geometry with N-bound thiazole. The crystals are monoclinic, space group $C2/c$, with cell dimensions a = 8.088 (3) Å, b = 14.964 (4) Å, c = 8.847 (2) Å, and Z = 4. Platinum has the expected square planar coordination with l(Pt–Cl) = 2.300 (5) Å and l(Pt–N) = 2.024 (18) and 2.077 (17) Å. Bond angles are normal with N(1)–Pt–N(2) = 180.0 (1)°, N(1)–Pt–Cl(1) = 904 (1)°, and N(2)–Pt–Cl(1A) = 89.6 (1)°. The intensity data were collected with Mo Kα radiation with λ = 0.710 73 Å. Refinement was by full-matrix least-squares methods to a final R value of 5.45%. The thiazole rings are not coplanar but slightly tilted to each other at an angle of 14.3°. The dihedral angles between the Pt coordination plane and the thiazole rings are 119.3 and 105.0°. The biological studies confirm the generality of activation of the trans geometry using planar ligands. Cytotoxicity tests in murine leukemia (L1210) cell lines both sensitive and rendered resistant to cisplatin show that the complexes show equivalent cytostatic activity to that of cisplatin. Thus the activity is an order of magnitude greater than *trans*-$[PtCl_2(NH_3)_2]$. The cytotoxicity is further marked by consistent activity in the cisplatin-resistant cell line. Contrary to the well-established but empirical structure–activity relationships, the trans geometry can give platinum complexes with cytotoxicity equivalent to that of the analogous cis isomer. The results point to a further source of platinum antitumor complexes acting by a different molecular mechanism to cisplatin with potential for antitumor activity complementary to that of the clinically used drug.

The clinical utility of platinum anticancer agents is by now well established.[1] The empirical structure–activity relationships delineated for platinum complexes state that the cis geometry, e.g. *cis*-$[PtX_2(NH_3)_2]$, where X = Cl or X_2 = 1,1-cyclobutanedicarboxylate, is necessary for antitumor activity. When the ammine is changed to a planar ligand such as pyridine (py) in *trans*-$[PtCl_2(py)_2]$, the cytotoxicity of the trans complex is dramatically enhanced in comparison to that of both its cis isomer and *trans*-$[PtCl_2(NH_3)_2]$, which is inactive at biologically relevant concentrations.[2] The generality of this effect has been studied

(1) Farrell, N. Transition Metal Complexes as Drugs and Chemotherapeutic Agents. In *Catalysis by Metal Complexes*; James, B. R., Ugo, R., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; Vol. 11, Chapter 2, pp 46–66.
(2) Farrell, N.; Ha, T. T. B.; Souchard, J.-P.; Wimmer, F. L.; Cros, S.; Johnson, N. P. *J. Med. Chem.* **1989**, *32*, 2240.

0020-1669/92/1331-0634$03.00/0