order of 1–2 cm^{-1}, vanishingly small compared to changes in bond energies and vibrational quanta which likely ensue following ligand substitution. It is likely that the changes reflect changes in the orbital energies on the Mn^{II} ion on going from a π acceptor ligand like pyridine in complex **1** to the relatively hard Lewis base H_2O in complex **2**. This change likely has an effect on the energetics of through-bond interactions but trying to associate energy changes of a few wavenumbers to these geometric changes would be tenuous at best. In actuality, we feel that the difficulty in accounting for such a small change in energy is one of the attractive features of our results. That is, we have observed that very minor changes in the energies of pairwise exchange interactions can lead to a change in the ground state of a complex.

The present results do lend some support to the assertions by Brudvig et al.[15] regarding the origins of the $g = 4.1$ and multiline $g \approx 2$ pattern from the OEC. Their model assigns both transitions as originating from the same tetranuclear complex, with changes in the conformation of the protein stabilizing or destabilizing a $S = {}^{1}/_{2}$ excited state relative to the $S = {}^{3}/_{2}$ ground state. We have shown it is possible to stabilize a $S = {}^{3}/_{2}$ ground state in a polynuclear Mn complex. Clearly, the oxidation states in complexes **1** and **2** bear little relation to what is likely present in S_2, but complex **1** is to our knowledge the first polynuclear Mn complex which has a well-characterized $S = {}^{3}/_{2}$ ground state. Perhaps more importantly with respect to PSII is that there are strong indications from this work that by making relatively minor changes in the periphery of an exchange-coupled complex it is possible to significantly alter the electronic structure of a complex even to the extent of changing the ground state.

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Supplementary Material Available: Tables of magnetic susceptibility data and variable-field magnetization data for $[Mn_3O(O_2CCH_3)_6(py)_3](py)$ (**1**) and magnetic susceptibility data for $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]\cdot{}^{1}/_{2}CH_3CN$ (**2**) (3 pages). Ordering information is given on any current masthead page.

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Dinuclear Complexes of Platinum with the 4,4′-Dipyrazolylmethane Ligand. Synthesis, Characterization, and X-ray Crystal Structure of γ-Bis(4,4′-dipyrazolylmethane-*N*,*N*′)bis[dichloroplatinum(II)]–*N*,*N*-Dimethylformamide (1/2) and Related Complexes

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The preparation and characterization of novel platinum complexes with the 4,4′-dipyrazolylmethane (dpzm) ligand is described. Some proposed conformational isomers of the square-planar, dinuclear platinum(II) complexes α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5dmf$, β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$, and γ-$[Cl_2Pt(dpzm)_2PtCl_2]\cdot2dmf$ and the corresponding octahedral platinum(IV) complexes α-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5H_2O$ and β-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5dmf\cdot0.5H_2O$ have been synthesized and characterized. Interconversion of the conformational forms for each oxidation state can be accomplished by various means. The mononuclear complexes *cis*-$[PtCl_2(dmf)(dpzmH)]Cl$ and *cis*-$[PtCl_4(dmf)(dpzmH)]Cl\cdot0.5dmf$ and dinuclear mixed-oxidation state complex $[Cl_4Pt(\mu\text{-dpzm})_2PtCl_2]$ were also prepared and characterized. The X-ray crystal structure determination of γ-$[Cl_2Pt(dpzm)_2PtCl_2]\cdot2dmf$ is reported. The complex exists as discrete molecular units with strong hydrogen-bonding to dmf solvent molecules. Each platinum atom is coordinated to two bridging dpzm ligands in a cis geometry. The crystals are monoclinic, space group $P2_1/n$, with cell parameters $a = 9.790$ (1) Å, $b = 13.444$ (2) Å, $c = 12.174$ (2) Å, $\beta = 105.74$ (1)°, and $Z = 2$. The structure was solved by the heavy-atom method and refined to $R = 0.036$ based on 2816 reflections.

Introduction

Apart from the work of Cuadro and others,[1] there have been no reports of complexes containing the 4,4′-dipyrazolylmethane (dpzm) ligand nor any studies of potential anticancer properties of its metal complexes. It is known that the ligand itself is not cytotoxic against HeLa cells in vitro.[2]

Dinuclear platinum(II) complexes have been described recently in a series of papers by Farrell et al.[3–7] These show very good anticancer activity including activity toward cisplatin-resistant cell lines. The complexes possess two platinum centers which are bridged by a single diamine ligand such as 1,4-butanediamine. In contrast, the present work describes two platinum centers linked by two bridging ligands. Both types of dinuclear complexes represent new classes of anticancer agents. Unlike the aliphatic diamines used by Farrell and co-workers, the dpzm ligand is forced to act as a bridging bidentate ligand, being unable to form a chelate ring involving the same metal center. Some new mononuclear complexes of platinum(II) and -(IV) have also been isolated from acid solutions employing conditions similar to those used by other workers.[8] The in vivo anticancer drug screening and unique in vitro DNA-binding results for a selected number of complexes will be reported subsequently.[9]

Experimental Section

Materials and Methods. Elemental analyses were performed by the Australian National University Microanalytical Service. Platinum was determined gravimetrically following decomposition of the complex in N_2/methanol vapor. Pyrazole, methylene bromide, and methyl iodide were obtained commercially (Aldrich). The ligand dpzm was prepared

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according to the literature procedure.[10] *N,N*-dimethylformamide (dmf) (May & Baker) was dried and purified by treatment with 4-Å molecular sieves for 24 h, followed by shaking with BaO for 48 h, and distillation under reduced pressure.[11] All other chemicals and organic solvents were LR or higher grade, and were used without further purification. $K_2[PtCl_4]$ was prepared by the methods of Keller[12] and Giedt and Nyman.[13]

Physical Measurements. NMR spectra were obtained by using a Varian XL200E Fourier transform NMR instrument (^1H at 200.0 MHz, ^{13}C at 50.3 MHz, and ^{195}Pt at 42.9 MHz) and 5-mm quartz tubes. A Varian CFT-20 (^1H at 80.0 MHz) Fourier transform NMR instrument was used for the measurement of $^{195}Pt-^1H$ coupling constants. Variable-temperature ^1H NMR experiments were performed on a Varian XR300 Fourier transform instrument (^1H at 300.0 MHz). The chemical shifts (δ) are in ppm for all NMR spectra, and dmf-d_7 (99 atom % D, Aldrich Chemical Co.) was used as the solvent unless specified. ^1H and ^{13}C chemical shifts are reported relative to internal tms (0 ppm), and ^{195}Pt shifts were referenced relative to an external solution of 0.1 M $Na_2[PtCl_6]$ in D_2O (0 ppm). All chemical shifts are positive to lower shielding, and the spectra of all nuclei (except ^1H) were ^1H-decoupled. For ^1H NMR spectra, the data are reported as follows: chemical shift, multiplicity of peaks (and coupling constants), number of protons, and assignment of protons. The calculated values for $^{195}Pt\{^1H\}$ NMR line widths ($\Delta\nu_{1/2}$) equal the width of the signals at half-height (in Hz) minus 5.0 Hz used for line-broadening (in the data processing). IR spectra (KBr disk, unless specified) were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer 683 grating infrared spectrophotometer (calibrated with polystyrene film) or a Perkin-Elmer 1600 series Fourier transform infrared spectrophotometer. Mass spectra were obtained by using the fast-atom bombardment (FAB) technique (Commonwealth Scientific and Industrial Research Organisation, Division of Chemicals and Polymers, Melbourne, Australia). The samples were dissolved in dmso prior to application on the sample stage. Glycerol, thioglycerol, or thiodiethylene glycol were used as matrices. Mass spectra of organic compounds were obtained by the electron-impact (EI) method on a VG Micromass 7070F mass spectrometer. UV spectra were recorded on a Shimadzu UV-160 spectrophotometer (solvent specified). Molar conductivities were measured by using a Philips GM4249 conductivity bridge, with sample concentrations of 10^{-3} M in an appropriate solvent (specified) at room temperature. X-ray powder diffraction patterns were recorded using an automatic Philips PW 1049 counter diffractometer (Philips PW 1010 generator) using Ni-filtered Cu Kα (λ = 1.5418 Å) radiation. Melting points (uncorrected) were obtained by means of an "electrothermal" digital melting-point apparatus.

Preparation of Compounds. (1,1′-Dimethyl-4,4′-dipyrazolyl)methane, Me_2dpzm. Methyl iodide (2.84 g, 0.020 mol), tetrabutylammonium bromide (0.065 g, 2.00 mmol), dpzm (0.740 g, 5.00 mmol), 50% (w/v) NaOH (10 mL), and toluene (50 mL) were placed in a 250-mL round-bottom flask provided with a reflux condenser. The mixture was stirred vigorously at 115 °C for 6 h and cooled to room temperature, and the two layers were allowed to separate. The toluene was discarded, and the aqueous phase was extracted with ethyl acetate (400 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent removed in vacuo to yield a yellow product (0.480 g), which was distilled (bp 180 °C, 1 mmHg) to give a colorless, oily liquid (0.410 g, 45.9%). Anal. Calcd for $C_9H_{12}N_4$: C, 61.34; H, 6.86; N, 31.79. Found: C, 60.70; H, 7.27; N, 31.64. IR (film/NaCl plates): 3450 (br s), 3145 (w), 3105 (w), 3097 (m), 2945 (s), 2860 (w), 1670 (br w), 1570 (m), 1442 (s), 1400 (s), 1362 (m), 1349 (w), 1320 (m), 1288 (m), 1225 (w), 1195 (w), 1170 (s), 1060 (w), 1022 (s), 990 (vs), 925 (w), 853 (s), 807 (m), 763 (s), 702 (w), 695 (w), 654 (m), 615 (m) cm^{-1}. ^1H NMR (dmso-d_6): δ 7.41 (s, 2 H, aromatic ring H-3), 7.29 (s, 2 H, aromatic ring H-5), 3.76 (d [J = 4.2 Hz], 6 H, CH_3), 3.57 (s, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (dmso-d_6): δ 138.00 (aromatic ring C-3), 128.86 (aromatic ring C-5), 120.62 (aromatic ring C-4), 38.28 (CH_3), 18.76 (CH_2). MS: *m/z* (relative % intensity) 176 (M^+, 100). UV (EtOH): 225.1 nm.

***catena*-Bis(μ-4,4′-dipyrazolylmethane-*N,N′*)platinum(II) Tetrachloroplatinate(II), $[Pt(\mu\text{-dpzm})_2]_n[PtCl_4]_n$.** A 0.50-g (1.2-mmol) amount of $K_2[PtCl_4]$ was dissolved in distilled water (5 mL) and the solution heated to approximately 50 °C. A solution of dpzm (0.18 g, 1.2 mmol) in boiling water (7 mL) was added to the solution and the mixture stirred for 0.5 h. The pale-green/yellow solid was collected by filtration and washed with distilled water (100 mL), absolute ethanol (30 mL), and finally diethyl ether (20 mL). Yield: 0.48 g (96%). Anal. Calcd for $C_{14}H_{16}Cl_4N_8Pt_2$: C, 20.30; H, 1.95; N, 13.53; Cl, 17.12. Found: C, 20.58; H, 1.75; N, 12.91; Cl, 17.25. IR (KBr disk): 3290 (vs vbr), 3117 (br s), 2957 (s), 2850 (m), 1618 (m), 1571 (w), 1484 (m), 1438 (w), 1407 (s), 1367 (m), 1297 (w), 1241 (w), 1127 (vs), 1083 (vs), 1010 (s), 977 (m), 919 (w), 859 (m), 836 (m), 747 (s), 718 (w), 670 (w), 601 (m), 325 (br s) cm^{-1}. X-ray diffraction pattern (Cu Kα radiation) was characteristic of an amorphous substance.

α-Bis(μ-4,4′-dipyrazolylmethane-*N,N′*)bis[dichloroplatinum(II)]–*N,N*-Dimethylformamide (2/1), α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf. A 4.16-g (10.0-mmol) amount of $K_2[PtCl_4]$ was added to distilled water (160 mL), and the pH of the solution was adjusted to 1.0 with HCl (12 M). The pH of a solution containing 1.48 g (10.0 mmol) of dpzm in hot (ca. 70 °C) water (120 mL) and acetone (40 mL) was likewise adjusted to 1.0 with HCl (12 M), and the two solutions were mixed and stirred at room temperature for 72 h. After this time, a pale-green/yellow solid (4.65 g) was collected by filtration, washed with water (30 mL), absolute ethanol (30 mL), and then ether (30 mL), and dried in vacuo for 12 h. The product was dissolved in dmf (110 mL), and ice-cold HCl (0.1 M) was added until the solution became cloudy. The mixture was allowed to stand at 2 °C for 3 h and then filtered. Yield of very pale-green/yellow solid: 1.16 g (26.9%). The filtrate was retained for the isolation of *cis*-$[PtCl_2$(dmf)(dpzmH)]Cl and β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$. Anal. Calcd for $C_{15.5}H_{19.5}Cl_4N_{8.5}O_{0.5}Pt_2$: C, 21.53; H, 2.27; N, 13.77; Pt, 45.12. Found: C, 21.05; H, 2.35; N, 13.48; Pt, 45.29. IR (KBr disk): 3292 (vs), 3189 (vs), 3118 (vs), 2986 (s), 2867 (m), 1651 (vs), 1570 (w), 1504 (w), 1486 (s), 1429 (m), 1410 (s), 1388 (m), 1374 (s), 1300 (w), 1242 (m), 1186 (w), 1126 (vs), 1085 (vs), 1010 (s), 1000 (s), 978 (m), 919 (m), 878 (m), 859 (w), 838 (s), 747 (s), 720 (m), 664 (m), 600 (m), 579 (m), 480 (br w), 330 (s), 322 (s) cm^{-1}. ^1H NMR (dmso-d_6): δ 13.67 (s, 4 H, N–H), 7.81 (s [$J_{^{195}Pt-^1H}$ = 10 ± 2 Hz], 4 H, aromatic ring H-5), 7.05 (s [$J_{^{195}Pt-^1H}$ = 21 Hz], 4 H, aromatic ring H-3), 3.58 (s, 4 H, CH_2); resonances attributed to dmf of crystallization occur at δ 8.04 (s, 1 H, formyl H), 2.95 (s, 3 H, CH_3), 2.75 (s, 3 H, CH_3). X-ray powder diffraction pattern (Cu Kα radiation) [2θ angle (relative intensity)]: 10.60 (84), 11.70 (23), 12.5 (100), 13.40 (35), 13.75 (49), 15.40 (61), 16.40 (29), 16.75 (49), 17.00 (41), 19.15 (71), 20.35 (69), 21.05 (46), 22.10 (49), 22.60 (35), 23.45 (26), 25.50 (27), 26.70 (25), 28.35 (69), 29.45 (22), 30.55 (35), 31.60 (38), 32.35 (30), 33.60 (22), 35.05 (25), 37.35 (30), 41.00 (21), 41.65 (23). Molar conductivity (in dmso, 20 °C): Λ_m = 2.5 S cm^2 mol^{-1}.

***cis*-Dichloro(*N,N*-dimethylformamide-*O*)(4,4′-dipyrazolylmethane-*N*)platinum(II) Hydrochloride, *cis*-$[PtCl_2$(dmf)(dpzmH)]Cl.** A 0.1 M HCl solution was added to the filtrate obtained above until the solution became cloudy. The mixture was cooled to 2 °C for 12 h, and the amber solid was collected, washed with 50% (v/v) dmf/H_2O, and dried as above. Yield: 2.12 g (40.5%). The filtrate was retained for the isolation of β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$. Anal. Calcd for $C_{10}H_{16}Cl_3N_5OPt$: C, 22.93; H, 3.08; N, 13.37; Pt, 37.25. Found: C, 22.44; H, 2.60; N, 13.85; Pt, 36.99. IR (KBr disk): 3350–3116 (vs vbr), 2922 (vs vbr), 2855 (m), 1641 (vs br), 1478 (m), 1435 (m), 1406 (m), 1385 (m), 1248 (m), 1124 (s), 1077 (s), 1008 (s), 973 (m), 922 (w), 858 (m), 747 (s), 662 (s), 588 (s), 330 (s), 320 (s) cm^{-1}. ^1H NMR (after 24 h in dmf-d_7 solution): δ 13.75 (br s, 1 H, N–H of coordinated aromatic ring), 13.35 (br s, 1 H, N–H), 8.13 (s, 1 H, formyl H of coordinated dmf), 7.95 (s, 1 H, H-5 of coordinated aromatic ring), 7.90 (s, 1 H, aromatic ring H-5), 7.48 (br m, 1 H, aromatic ring H-3), 7.21 (s [$J_{^{195}Pt-^1H}$ = 23 ± 1 Hz], 1 H, H-3 of coordinated aromatic ring), 3.77 (s, 2 H, CH_2), 2.96 (s, 3 H, CH_3 of coordinated dmf), 2.79 (s, 3 H, CH_3 of coordinated dmf). $^{195}Pt\{^1H\}$ NMR (after 24 h in dmf-d_7 solution): δ −1885. $^{13}C\{^1H\}$ NMR (after 24 h in dmf-d_7 solution): δ 140.53 (aromatic ring C-3), 139.76 (C-3 of coordinated aromatic ring), 131.19 (aromatic ring C-5), 130.81 (C-5 of coordinated aromatic ring), 122.13 (C-4 of coordinated aromatic ring), 121.71 (aromatic ring C-4), 19.06 (CH_2). (After a period of several days, there is a substantial increase in the intensity of resonances at δ 13.75, 7.95, 7.21, and 3.77 with the simultaneous appearance of a new peak at δ 3.73 in the ^1H NMR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum, the peaks at δ 139.76, 130.81, and 122.13 also increase in intensity, with the appearance of a new peak at δ 18.90. In addition, a resonance at δ −1896 appears in the $^{195}Pt\{^1H\}$ NMR spectrum. These changes in the NMR spectra are attributed to the presence of β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$ in solution.) X-ray diffraction pattern (Cu Kα radiation) [2θ angle (relative intensity)]: this was characteristic of an amorphous substance, with very broad peaks at ca. 12 (100) and 22 (100). Molar conductivity (in dmso, 20 °C): Λ_m = 8.4 S cm^2 mol^{-1}.

β-Bis(μ-4,4′-dipyrazolylmethane-*N,N′*)bis[dichloroplatinum(II)], β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$. HCl (0.1 M) was added to the filtrate obtained above until the solution became cloudy. The mixture was cooled to 2 °C for 12 h to give a pale yellow solid, which was filtered off, washed, and dried as above for the α complex. Yield: 1.10 g. The solid was suspended in dmf (10 mL) and the mixture stirred at room temperature for 12 h. A pale-green/yellow solid was filtered off (0.48 g, 11.1%) and identified as α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf. Addition of 0.1 M HCl

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to the filtrate gave a pale yellow solid, which was collected, washed, and dried as described for α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5dmf$. Yield: 0.58 g (14.0%). Anal. Calcd for $C_{14}H_{16}Cl_4N_8Pt_2$: C, 20.30; H, 1.95; N, 13.53; Pt, 47.11. Found: C, 20.42; H, 1.98; N, 13.29; Pt, 47.13. IR (KBr disk): 3488 (br vs), 3285 (br vs), 3122 (br vs), 2973 (s), 2862 (s), 1618 (m), 1577 (w), 1481 (m), 1438 (m), 1407 (s), 1367 (m), 1297 (w), 1243 (w), 1130 (vs), 1082 (vs), 1010 (s), 1003 (sh), 977 (m), 921 (w), 864 (m), 833 (m), 747 (s), 670 (m), 593 (s), 472 (br w), 330 (s), 323 (s) cm^{-1}. ^1H NMR: δ 13.75 (s, 4 H, N–H), 7.99 (s $[J_{^{195}Pt-^1H} = 11 \pm 2\ Hz]$, 4 H, aromatic ring H-5), 7.20 (s $[J_{^{195}Pt-^1H} = 24\ Hz]$, 4 H, aromatic ring H-3), 3.73 (s, 4 H, CH_2). $^{195}Pt\{^1H\}$ NMR: δ −1896. $^{13}C\{^1H\}$ NMR: δ 139.79 (aromatic ring C-3), 130.84 (aromatic ring C-5), 122.16 (aromatic ring C-4), 18.87 (CH_2). X-ray powder diffraction pattern (Cu Kα radiation) [2θ angle (relative intensity)]: 10.50 (49), 11.70 (29), 12.45 (69), 13.30 (63), 13.65 (62), 15.30 (80), 16.35 (46), 16.65 (68), 19.05 (100), 19.50 (37), 20.20 (94), 20.95 (45), 22.55 (36), 24.10 (32), 25.45 (33), 26.60 (31), 27.75 (43), 28.30 (57), 30.25 (43), 32.20 (29), 36.95 (34), 45.35 (28). Molar conductivity (in dmf, 18 °C): $\Lambda_m = 6.5\ S\ cm^2\ mol^{-1}$. FABMS (after ca. 2 days in dmso solution): Quasi-molecular-ion $(M - 1)^+$ cluster centered at m/z 912 corresponding to (β-$[Cl(dmso)Pt(\mu\text{-dpzm})_2PtCl(dmso)] - H)^+$.

α-Bis(μ-4,4′-dipyrazolylmethane-*N*,*N*′)bis[tetrachloroplatinum(IV)]–Water (2/1), α-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5H_2O$. To 4.00 g (7.72 mmol) of $H_2[PtCl_6]\cdot6H_2O$ in distilled water (200 mL) was added 1.14 g (7.69 mmol) of dpzm in an equal volume of hot (70 °C), distilled water, and the mixture was stirred at room temperature for 72 h. A bright yellow, microcrystalline solid was collected by filtration, washed, and dried as described above for the α complex. Yield: 3.51 g. The product was dissolved in 40 mL of ice-cold dmf. A 0.1 M HCl solution was added until the solution became cloudy, and the mixture was cooled at 2 °C for 3 h. A lemon-yellow solid was filtered off and washed and dried as above. Yield: 0.29 g (7.7%). The filtrate was retained for the isolation of other products. Anal. Calcd for $C_{14}H_{17}Cl_8NO_{0.5}Pt_2$: C, 17.17; H, 1.75; N, 11.44; Pt, 39.85. Found: C, 17.68; H, 1.85; N, 11.46; Pt, 40.03. IR (KBr disk): 3608 (s), 3538 (s), 3276 (vs), 3126 (s), 2955 (w), 2859 (w), 1623 (vs), 1482 (s), 1440 (w), 1407 (m), 1369 (s), 1303 (w), 1252 (m), 1121 (vs), 1088 (vs), 1007 (s), 999 (m), 973 (w), 922 (w), 862 (m), 826 (w), 746 (m), 718 (w), 676 (m), 623 (w), 602 (w), 584 (m), 504 (w), 425 (br w), 354 (s), 343 (s), 334 (s) cm^{-1}. ^1H NMR: δ 13.91 (s, 4 H, N–H), 8.26 (s $[J_{^{195}Pt-^1H} = 6.9\ Hz]$, 4 H, aromatic ring H-5), 7.77 (s $[J_{^{195}Pt-^1H} = 10.7\ Hz]$, 4 H, aromatic ring H-3), 3.55 (br s, H_2O), 3.91 (s, 4 H, CH_2). $^{195}Pt\{^1H\}$ NMR: δ +153. $^{13}C\{^1H\}$ NMR: δ 139.34 (aromatic ring C-3), 133.70 (aromatic ring C-5), 123.09 (aromatic ring C-4), 19.06 (CH_2). X-ray powder diffraction pattern (Cu Kα radiation) [2θ angle (relative intensity)]: 8.15 (14), 11.90 (65), 12.70 (73), 14.90 (26), 16.20 (100), 16.90 (29), 17.55 (33), 18.20 (20), 18.50 (23), 20.00 (14), 21.05 (27), 25.35 (40), 26.70 (25), 32.50 (16), 33.45 (15), 34.30 (20), 35.45 (15), 36.75 (11), 40.90 (14). Molar conductivity (in dmf, 19 °C): $\Lambda_m = 3.9\ S\ cm^2\ mol^{-1}$.

***cis*-Tetrachloro(*N*,*N*-dimethylformamide-*O*)(4,4′-dipyrazolylmethane-*N*)platinum(IV) Hydrochloride–*N*,*N*-Dimethylformamide (2/1), *cis*-$[PtCl_4(dmf)(dpzmH)]Cl\cdot0.5dmf$.** The ice-cold filtrate obtained from the procedure described for α-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5H_2O$ was treated with 0.1 M HCl until the solution became cloudy, and the mixture was cooled at 2 °C for 24 h. A bright yellow precipitate was collected, washed with the minimum volume of 50% (v/v) dmf/water, and dried in vacuo at 100 °C for 6 h. Yield: 1.24 g (25.5%). The filtrate was kept for the isolation of further products. Anal. Calcd for $C_{11.5}H_{19.5}Cl_5N_{5.5}O_{1.5}Pt$: C, 21.88; H, 3.11; N, 12.21; Pt, 30.91. Found: C, 21.41; H, 2.44; N, 12.88; Pt, 30.62. IR (KBr disk): 3348–2900 (vs vbr), 3121 (vs vbr), 1653–1635 (vs), 1478 (m), 1434 (m), 1406 (m), 1370 (s), 1247 (m), 1121 (s), 1088 (vs), 1005 (m), 974 (m), 834 (m), 745 (m), 662 (m), 600 (m), 340 (s), 333 (s), 318 (s) cm^{-1}. ^1H NMR: δ 14.00 (br s, 1 H, N–H of coordinated aromatic ring), 13.40 (br s, 1 H, N–H), 8.27 (s, 1 H, H-5 of coordinated aromatic ring), 8.22 (br m, 1 H, aromatic ring H-3), 8.20 (s, 1 H, aromatic ring H-5), 8.17 (s, 1 H, formyl H of coordinated dmf), 7.61 (s, 1 H, H-3 of coordinated aromatic), 4.09 (s, 1 H, CH_2), 2.95 (s, 3 H, CH_3 of coordinated dmf), 2.79 (s, 3 H, CH_3 of coordinated dmf). $^{195}Pt\{^1H\}$ NMR: δ +15. X-ray diffraction pattern (Cu Kα radiation) [2θ angle (relative intensity)]: the spectrum was characteristic of an amorphous substance, with very broad peaks located at ca. 10 (100) and 19 (97). Molar conductivity (in dmf, 24 °C): $\Lambda_m = 12.4\ S\ cm^2\ mol^{-1}$.

β-Bis(μ-4,4′-dipyrazolylmethane-*N*,*N*′)bis[tetrachloroplatinum(IV)]–*N*,*N*-Dimethylformamide–Water (2/1/1), β-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5dmf\cdot0.5H_2O$. A 0.1 M HCl solution was added to the clear, yellow filtrate obtained from the previous preparation until the solution became cloudy, and the mixture was cooled to 2 °C for 24 h. A bright yellow solid was filtered off and washed as for the α complex above. Yield: 1.67 g. The product was added to ice-cold dmf (10 mL) and filtered to remove a small amount of lemon-yellow solid (0.22 g, 5.8%) identified as α-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5H_2O$ from analytical and spectroscopic data. A 0.1 M HCl solution was added to the filtrate to cloudiness, and after cooling of the mixture to 2 °C for 12 h, a bright yellow solid was filtered off, washed, and dried as above. Yield: 1.39 g (35.9%). Anal. Calcd for $C_{15.5}H_{20.5}Cl_8N_{8.5}OPt_2$: C, 18.33; H, 2.03; N, 11.72; Cl, 27.92; Pt, 38.42. Found: C, 18.26; H, 1.92; N, 11.80; Cl, 27.92; Pt, 38.48. IR (KBr disk): 3608 (s), 3539 (s), 3276 (vs), 3126 (vs), 2955 (s), 2858 (w), 1654 (s), 1623 (vs), 1481 (vs), 1440 (w), 1406 (m), 1369 (s), 1348 (w), 1303 (w), 1253 (m), 1121 (vs), 1087 (vs), 1007 (s), 999 (m), 973 (w), 922 (w), 862 (m), 826 (w), 746 (m), 718 (w), 676 (m), 623 (w), 602 (m), 583 (m), 452 (w br), 355 (s), 344 (s), 336 (s) cm^{-1}. ^1H NMR (dmf-d_7): δ 13.92 (br s, 4 H, N–H), 8.27 (s $[J_{^{195}Pt-^1H} = 6.9\ Hz]$, 4 H, aromatic H-5), 7.78 (s $[J_{^{195}Pt-^1H} = 10.6\ Hz]$, 4 H, aromatic ring H-3), 3.91 (s, 4 H, CH_2), 3.55 (br s, H_2O). $^{195}Pt\{^1H\}$ NMR: δ +148. $^{13}C\{^1H\}$ NMR: δ 139.38 (aromatic ring C-3), 133.72 (aromatic ring C-5), 123.12 (aromatic ring C-4), 19.08 (CH_2). X-ray powder diffraction pattern (Cu Kα radiation) [2θ angle (relative intensity)]: 8.05 (9), 12.10 (8), 12.80 (16), 16.30 (100), 16.90 (21), 25.20 (15), 26.70 (13), 32.70 (13), 33.35 (10), 34.30 (11). Molar conductivity (in dmf, 22 °C): $\Lambda_m = 7.2\ S\ cm^2\ mol^{-1}$.

Hexachloro-1κ^4,2κ^2-bis(μ-4,4′-dipyrazolylmethane-1κ*N*:2κ*N*′)-1-platinum(IV)-2-platinum(II), $[Cl_4Pt(\mu\text{-dpzm})_2PtCl_2]$. A 0.204-g (0.201-mmol) amount of β-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5dmf\cdot0.5H_2O$ was dissolved in dmf (15 mL). A 0.010-g (0.095-mmol) amount of $N_2H_4\cdot2HCl$ in distilled water (5 mL) was added to the solution, and the mixture was heated to 100 °C for 3 h. The volume of liquid was then reduced in vacuo to ca. 5 mL, and 0.1 M HCl was added until the solution became cloudy. On cooling of the mixture to 2 °C for 48 h, a pale orange/yellow solid was deposited in the flask. The product was filtered off, washed with the minimum volume of 50% (v/v) dmf/water, followed by water (20 mL), absolute ethanol (20 mL), and diethyl ether (20 mL), and dried in vacuo at 100 °C for 6 h. Yield: 0.08 g (46.8%). Anal. Calcd for $C_{14}H_{16}Cl_6N_8Pt_2$: C, 18.70; H, 1.79; N, 12.46; Pt, 43.49. Found: C, 18.84; H, 1.82; N, 12.26; Pt, 43.08. IR (KBr disk): 3300 (vs vbr), 3122 (vbr vs), 2940 (s), 2870 (w), 1482 (s), 1436 (s), 1407 (s), 1385 (s), 1294 (m), 1252 (m), 1127 (vs), 1089 (vs), 1009 (s), 1002 (sh), 975 (m), 922 (w), 862 (m), 832 (m), 747 (s), 663 (m), 605 (m br), 345 (s), 338 (br s), 330 (br s), 325 (sh) cm^{-1}. ^1H NMR: δ 14.00 (br s, 2 H, N–H), 13.40 (br s, 2 H, N–H), 8.20 (br s, 4 H, aromatic ring H-5), 7.60 (br s, 4 H, aromatic ring H-3), 3.79 (br s, 2 H, CH_2). $^{195}Pt\{^1H\}$ NMR: δ +154 (br), −1893 (br). Molar conductivity (in dmf, 21 °C): $\Lambda_m = 6.9\ S\ cm^2\ mol^{-1}$.

Bis[μ-1,1′-dimethyl-4,4′-dipyrazolylmethane-*N*,*N*′]bis[dichloroplatinum(II)]–*N*,*N*-Dimethylformamide (2/1), $[Cl_2Pt(\mu\text{-}Me_2dpzm)_2PtCl_2]\cdot0.5dmf$. $K_2[PtCl_4]$ (0.208 g, 0.501 mmol) was dissolved in water (16 mL) and the pH adjusted to 1.0 with HCl (12 M). Me_2dpzm (0.088 g, 0.493 mmol) in hot water (12 mL, 70 °C) was likewise adjusted to pH 1.0, and the two solutions were mixed and stirred at room temperature for 72 h. A yellow solid (0.20 g) was collected by filtration, the solid was dissolved in ice-cold dmf (20 mL), and 0.1 M HCl was added until the solution became cloudy. After cooling of the mixture to 2 °C for 24 h, an orange solid was obtained in low yield (0.02 g) and discarded. Further addition of 0.1 M HCl to the ice-cold filtrate until the solution became cloudy, and cooling of the mixture to 2 °C for 24 h, gave a light-yellow solid, which was collected by filtration, washed as previously described, and dried at 100 °C for 6 h. Yield: 0.120 g (64.4%). Anal. Calcd for $C_{19.5}H_{27.5}Cl_4N_{8.5}O_{0.5}Pt_2$: C, 25.43; H, 3.01; N, 12.93; Cl, 15.40; Pt, 42.37. Found: C, 25.16; H, 2.81; N, 12.53; Cl, 15.31; Pt, 42.21. IR (KBr disk): 3111 (vs), 2938 (m), 2855 (w), 1657 (s), 1617 (m), 1573 (w), 1485 (w), 1441 (vs), 1410 (s), 1368 (m), 1327 (w), 1296 (s), 1209 (w), 1166 (vs), 1056 (s), 1021 (m), 987 (w), 919 (w), 829 (m), 763 (s), 699 (m), 636 (m), 608 (m), 451 (br w), 327 (s), 318 (s) cm^{-1}. ^1H NMR (dmso-d_6): δ 7.90 (s, 2 H, aromatic ring H-5), 7.86 (br *m*, 2 H, aromatic ring H-3), 4.17 (m $[J_{H-H} = 5.8\ Hz, J_{^{195}Pt-^1H} = 11 \pm 2\ Hz]$, 6 H, CH_3), 3.57 (s, 2 H, CH_2). Molar conductivity (in dmso, 21 °C): $\Lambda_m = 5.5\ S\ cm^2\ mol^{-1}$.

Crystallography. Crystals of γ-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot2dmf$ were obtained by slow cooling of a hot, concentrated solution of the α complex in dmf. A crystal of approximate dimensions of 0.2 × 0.25 × 0.1 mm, with b along the diffractometer ϕ axis, was used to collect unit cell and intensity data. Unit cell dimensions were obtained by least-squares refinement from the settings of 25 high-angle reflections ($34° < 2\theta < 48°$) centered on a Philips PW1100/20 automatic four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å).

Crystal data: $C_{14}H_{16}Cl_4N_8Pt_2\cdot2C_3H_7NO$; $M_r = 974.54$; monoclinic, space group $P2_1/n$;[14] $a = 9.790$ (1), $b = 13.444$ (1), $c = 12.174$ (1) Å; $\beta = 105.74$ (1)°; $V = 1542.6$ Å^3; $F(000) = 920$; $Z = 2$; $D_c = 2.09\ g\ cm^{-3}$;

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[14] *International Tables for Crystallography*; Hahn, T., Ed.; D. Reidel: Dordrecht, The Netherlands, 1983; Vol. A, p 177.

Table I. ^{1}H, $^{13}C\{^{1}H\}$, and $^{195}Pt\{^{1}H\}$ NMR Data (δ, ppm) for Platinum Complexes of dpzm and Me_2dpzm (Except for Solvents of Crystallization) and for free dpzm and Me_2dpzm

	$\delta(^{1}H)$						$\delta(^{13}C)$				
compd	N-H	H-5	H-3	$-CH_2-$	HC(O)[d]	$-CH_3$	C-3	C-4	C-5	$-CH_2-$	$\delta(^{195}Pt)$
dpzm[a]	12.66	7.49	7.49	3.71			133.07	120.65	133.07	19.23	*e*
Me_2dpzm[b]	*e*	7.29	7.41	3.57	*e*	3.76[h]	138.00	120.62	128.86	18.76	*e*
α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf[b]	13.67	7.81 (10 ± 2)[g]	7.05 (21)[g]	3.58	*e*	*e*	*c*	*c*	*c*	*c*	*c*
β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$[a]	13.75	7.99 (11 ± 2)[g]	7.20 (24)[g]	3.73	*e*	*e*	139.79	122.16	130.84	18.87	−1896
cis-$[PtCl_2(\text{dmf})(\text{dpzmH})]Cl$[a]	13.75 13.35[f]	7.95 7.90[f]	7.21 7.48[f]	3.77	8.13	2.96[d] 2.79[d]	139.75 140.53[f]	122.16 121.70[f]	130.84 131.19[f]	19.06	−1885
α-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5H_2O$[a]	13.91	8.26 (6.9)[g]	7.77 (10.7)[g]	3.91	*e*	*e*	139.34	123.09	133.70	19.06	+153
β-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5\text{dmf}\cdot0.5H_2O$[a]	13.92	8.27 (6.9)[g]	7.78 (10.6)[g]	3.91	*e*	*e*	139.38	123.12	133.72	19.08	+148
cis-$[PtCl_4(\text{dmf})(\text{dpzmH})]Cl\cdot0.5$dmf[a]	14.00 13.40[f]	8.27 8.20[f]	7.61 8.22[f]	4.09	8.22	2.95[d] 2.79[d]					+15
$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_2]$[a]	13.40[i] 14.00[i]	8.20[i]	7.60[i]	3.79[i]	*e*	*e*					+154[i] −1893[i]
$[Cl_2Pt(\mu\text{-}Me_2\text{dpzm})_2PtCl_2]\cdot0.5$dmf[b]	*e*	7.90	7.86	3.57	*e*	4.17[h] (11 ± 2)[g]					

[a] In dmf-d_7. [b] In dmso-d_6. [c] Not obtained owing to poor solubility in dmf-d_7. [d] Coordinated dmf. [e] Not applicable. [f] Free pyrazole-type ring. [g] $^{195}Pt-^{1}H$ coupling (Hz). [h] *N*-methyl resonance. [i] Broad signal.

$D_m = 2.05$ g cm^{-3} (by flotation in bromoform/chloroform mixture); $\mu = 99.10$ cm^{-1} (Mo Kα).

Collection and Processing of Intensity Data. Data were collected at 20 °C on a Philips PW1100/20 diffractometer, with graphite-monochromated Mo Kα radiation, in the $\theta-2\theta$ scan mode with 2θ scan width of $1.2 + 0.34 \tan\theta$, scan speed 1.5° min^{-1}, and total background counting time 20 s. Three check reflections measured every 2 h showed approximately isotropic crystal decay of ca. 3%; the data were rescaled accordingly. Of 3880 reflections measured ($\pm h, +k, +l$; $2\theta_{max} = 60°$), 2816 unique, with $I \geq 3\sigma(I)$, were treated as "observed". Intensities were converted to structure factors in the usual way, and an analytical absorption correction was applied (transmission factor range 0.158–0.426).

Structure Solution and Refinement. Platinum atoms were located from a Patterson distribution, and the chlorine atoms from a difference Fourier synthesis. Further difference syntheses phased by the platinum and chlorine atoms revealed the carbon and nitrogen atoms of the dpzm ligand. Positional and anisotropic thermal parameters of all atoms in γ-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$ were refined by full-matrix least-squares calculations, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1$ in the early stages and $w = 1/[\sigma^2 + 0.25(pF_o)^2]$ (where $p = 0.03$) in the final cycles. An anomalous dispersion correction for all atoms was applied, and a Fourier map, calculated after several cycles of refinement, revealed the positions of the non-hydrogen atoms of the dmf molecule ($R = 0.073$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$). A subsequent difference synthesis revealed the location of the remaining non-hydrogen atoms of the dmf molecule. The positions of the hydrogen atoms could not be located from difference Fourier maps, and hydrogen atoms in calculated positions were included in the scattering model. The hydrogen atoms, in positions calculated with C–H and N–H equal to 0.95 Å, were assigned isotropic thermal parameters 10% greater than the values of the "equivalent" isotropic temperature factors (B_{eq}) of the carbon and nitrogen atoms to which they were bonded. All subsequent least-squares refinement calculations included the hydrogen atoms, but these parameters were not refined. The *R*-factor at this stage was 0.040. A substantial difference between the observed and calculated structure factors of some low-angle reflections was evident, and this discrepancy was attributed to a secondary extinction effect.[15] Therefore, a correction using the Zachariasen equation[16] was included in the model. The final refinement converged to $R = 0.036$, and weighted residual factor $R_w = 0.051$ ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{0.5}$). A final difference Fourier synthesis revealed no residual electron density greater than 1.01 e Å^{-3}. The structure solution and refinement of the complex were performed on a VAX-11/785 computer of the Australian National University Computer Services Centre, using the ANUCRYS crystallographic program library.[17,18]

Table II. ^{1}H NMR Data for α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf and β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$ in dmso-d_6 at 300 MHz

proton	δ(α)[a]	δ(β)[b]	proton	δ(α)[a]	δ(β)[b]
N-H[c]	13.670	13.670	H-3[d]	7.052	7.057
H-5[c]	7.811	7.813	$-CH_2-$[c]	3.585	3.586

[a] Chemical shifts (ppm) for α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf (±0.001 ppm). [b] Chemical shifts (ppm) for β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$ (±0.001 ppm). [c] No discernible "splitting" of these signals when a 1:1 molar mixture of α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf and β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$ was used: δ(N–H) = 13.670, δ(H-5) = 7.812, and δ($-CH_2-$) = 3.586. [d] Two distinct signals of approximately equal intensity were observed for this proton when a 1:1 molar mixture of α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf and β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$ was used.

Results

Infrared Studies. The IR spectra for each of the new complexes are consistent with the formulations given. The bands reported may be assigned to the ν(N–H) modes at ca. 3200–3350 cm^{-1}, and the remainder to various dpzm skeletal vibrations. The α-form also shows the ν(C=O) band expected for the presence of dmf. For the β-form, the shape of the 3200–3350-cm^{-1} band is broad with less structure than that for the α-form. This may reflect the presence of different conformational isomers and, for the α-form, the presence of hydrogen-bonding with the carbonyl group of dmf. Prolonged stirring with D_2O produced some N–H group exchange (new sharp bands at 2466 and 2398 cm^{-1}), but surprisingly a similar experiment with the β-form did not lead to exchange even after 2 weeks of stirring.

For the platinum(II) complexes, a cis stereochemistry is indicated by the presence of two strong bands at ca. 330 and 320 cm^{-1} attributed to ν(Pt–Cl). In the platinum(IV) complexes there are three bands in the Pt–Cl region (ca. 354, 343, and 334 cm^{-1}). Although four bands would be expected for a cis arrangement of the N-donor ligands,[19] band overlap precludes a detailed analysis of this region. For $[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]$ the α-form has 0.5 H_2O and the β-form 0.5 H_2O and 0.5 dmf of crystallization. Also, the water ν(OH) bands are very sharp (at 3608 and 3538 cm^{-1}) for these complexes. In the mixed-oxidation state/mixed-coordination number complex $[Cl_4Pt(\mu\text{-dpzm})_2PtCl_2]$ up to five bands may be expected but instead there are four bands in the Pt–Cl region and it is most likely that some band overlap occurs.

The mononuclear platinum(II) and platinum(IV) complexes display very broad bands in the 3350–2900-cm^{-1} region in agreement with the presence of combined N–H and N–H^{+} absorptions of a protonated dpzm ligand. Also there is a broad band at 1653–1635 cm^{-1} consistent with an O-bonded dmf ligand.

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NMR Studies. Relevant NMR (^1H, $^{13}C\{^1H\}$, $^{195}Pt\{^1H\}$) data for the novel complexes prepared in this work are provided in Tables I and II. The ^1H NMR spectra of α-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$]·0.5dmf and β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$] support their proposed structures. The poor solubility of α-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$]·0.5dmf in dmf-d_7 made it necessary to record the ^1H NMR spectra in dmso-d_6. In order to avoid any complications arising from extensive solvolysis of the complex by this solvent, the NMR solution was made up at room temperature just prior to recording the spectra.

The presence of $^{195}Pt-^1H$ coupling facilitates interpretation of the spectra since the ^{195}Pt isotope ($I = {}^1/_2$) is sufficiently abundant (33.7%) to give satellite signals. For β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$] in dmf-d_7, the sharp signal at δ 7.20 is assigned to the H-3 proton owing to its large $^{195}Pt-^1H$ coupling constant (24 Hz). The downfield signal, with a smaller coupling constant of 11 ± 2 Hz, at δ 7.99 is assigned to the H-5 proton. The resonance which is attributed to the methylene bridge protons is located at δ 3.73. A relatively sharp N–H resonance for β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$] in dmf-d_7 occurs downfield at δ 13.75. The sharpness of the N–H resonance and the absence of any discernible splitting in the adjacent H-5 resonance may be indicative of the rapid rate of exchange of the proton on the nitrogen atom; the N–H proton is decoupled from the nitrogen atom and from the adjacent H-5 proton. The addition of a drop of D_2O to the solution of the complex results in the loss of the N–H signal due to proton exchange. The chemical shifts for the protons of β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$] are slightly solvent dependent and move approximately 0.1 ppm upfield upon changing the solvent from dmf-d_7 to dmso-d_6. The signals for α-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$]·0.5dmf in dmso-d_6 can be assigned as described for β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$].

The sharp resonances observed for the dinuclear complexes are consistent with the sterically-hindered rotation of the pyrazole-type rings around the methylene bridge. On increase of temperature of a dmf-d_7 solution of β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$], the N–H resonance becomes appreciably broader and shifts upfield (ca. 0.5 ppm) until at 80 °C it is barely visible at approximately δ 13.5. The other peaks in the spectrum remain sharp, and it can be concluded that the changes associated with the N–H resonance are due to a $^{14}N-^1H$ decoupling mechanism and not to conformational changes involving the dpzm ligand. Further, the spectrum of β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$] in dmf-d_7 remains unchanged after several weeks in solution, the 16-membered ring structure of the complex being preserved in this solvent. In contrast, the complex undergoes extensive changes in dmso after this time.

A ^1H NMR experiment was performed in order to determine if there were any discernible differences in the molecular structures of α-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$]·0.5dmf and β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$] (Table II). Although the spectrum of a 1:1 molar mixture of the two complexes in dmso-d_6 displayed no significant differences in the chemical shifts of the N–H, H-5, and methylene protons, *two distinct signals* were observed for the H-3 proton. This is conclusive evidence that the two complexes are not identical (we thank a reviewer for suggesting this experiment). Differences in the orientation of the dpzm pyrazole-type ligands relative to the platinum coordination plane, albeit quite subtle (as judged from the very small separation of the two signals), are consistent with the NMR results of this experiment. This conclusion is supported by other physical and chemical data for the two complexes (see Discussion).

The $^{13}C\{^1H\}$ NMR spectrum of β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$] in dmf-d_7 reveals four resonances, three of which appear further downfield than the resonance at δ 18.87. This signal is attributed to the methylene carbon. The three remaining signals are assigned to the carbon atoms of the pyrazole-type moiety. These cannot be assigned unambiguously as $^{195}Pt-^{13}C$ couplings are not observed in this spectrum. However, by using 2-D heteronuclear chemical-shift correlation data obtained by Cinellu et al.[20] for the mononuclear complex *cis*-[$PtCl_2(Hpz)_2$], the ring carbon resonances can be assigned tentatively. The peak at δ 139.79 is assigned to C-3, and the upfield resonance at δ 130.84 is assigned to C-5. The remaining signal at δ 122.16 is then due to C-4.

The presence of a single resonance at δ −1896 in the $^{195}Pt\{^1H\}$ NMR spectrum of β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$] is indicative of *cis*-N_2Cl_2 type coordination[21,22] and is in the range of other platinum(II) complexes such as *cis*-[$PtCl_2(NH_3)_2$] (δ −2048 in dmf-d_7).[23] A single resonance, albeit broad due to the unresolvable coupling of quadrupolar ^{14}N to ^{195}Pt ($\Delta\nu_{1/2} \approx 325$ Hz), is indicative of the identical environments of two platinum(II) centers in β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$]. Unfortunately, the poor solubility in dmf-d_7 of α-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$]·0.5dmf precluded comparative measurements.

The ^1H NMR spectrum of *cis*-[$PtCl_2$(dmf)(dpzmH)]Cl possesses features which are similar to those found in the spectra of α-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$]·0.5dmf and β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$]. The resonances at δ 13.75 (N–H), 7.95 (H-5), 7.21 (H-3), and 3.77 (CH_2) are characteristic of a coordinated dpzm, as described for the dinuclear complexes. Other resonances at δ 13.35 (N–H), 7.90 (H-5), and 7.48 (H-3) have been assigned to the protonated, dangling pyrazole-moiety of dpzm. The multiplicity and broadness of the last mentioned signal is attributed to the adjacent, protonated N-2. No signal was observed for this proton, probably due to its inherent broadness. The resonances at δ 8.13 (formyl H), 2.96 (CH_3), and 2.79 (CH_3) are assigned to the coordinated dmf molecule. The downfield shifts of the peaks, when compared to those of free dmf, are in agreement with the findings of other workers,[24,25] who prepared and characterized the O-bonded dmf complexes *cis*-[$PtCl_2$(dmf)(L)] (where L = pyridine, picoline, and lutidine). They concluded that the oxygen atom of dmf was coordinated to platinum on the basis of the $^{195}Pt-^1H$ coupling constant of ca. 40 Hz for the downfield resonance assigned to the formyl proton. A similar coupling could not be discerned in the spectrum of *cis*-[$PtCl_2$(dmf)(dpzmH)]Cl due to the complexity of the δ 7.0–8.2 region. However, as the two upfield methyl resonances do not display any ^{195}Pt satellite peaks, it can be assumed that nitrogen is not the donor atom.[26] These conclusions are also consistent with the IR data of *cis*-[$PtCl_2$(dmf)(dpzmH)]Cl.

The $^{13}C\{^1H\}$ NMR spectrum of *cis*-[$PtCl_2$(dmf)(dpzmH)]Cl displays resonances at δ 139.76 (C-3), 130.81 (C-5), and 122.13 (C-4) corresponding to the coordinated pyrazole-type ring. The signal at δ 19.06 is assigned to the methylene bridge carbon atom, and the signals at δ 140.53 (C-3), 121.70 (C-5), and 131.19 (C-4) are attributed to the carbon atoms of the free pyrazole-type ring. These assignments are based on assumptions described for the corresponding dinuclear complexes. The resonances of coordinated dmf could not be located, and either they are masked by the dmf-d_7 resonances or have undergone dmf exchange reactions.

The presence of a single resonance at δ −1885 in the $^{195}Pt\{^1H\}$ NMR spectrum is consistent with the *cis*-[$PtCl_2$(dmf)(dpzmH)]Cl formulation. The downfield shift of this peak, compared with that found at δ − 1896 for β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$], is indicative of the replacement of a nitrogen donor ligand (dpzm) with an oxygen donor (dmf).[23]

The ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra of *cis*-[$PtCl_2$(dmf)(dpzmH)]Cl display significant changes after the complex has aged in dmf-d_7 solution for several days. This is in sharp contrast to the NMR spectrum of β-[$Cl_2Pt(\mu$-dpzm)$_2PtCl_2$], which is unchanged over this time in dmf. There is a substantial increase in intensity of the resonances at δ 13.75 (N–H), 7.95 (H-5), and 7.21 (H-3) in the ^1H NMR spectrum and δ 139.76 (C-3), 130.81 (C-5), and 122.13 (C-4) in the $^{13}C\{^1H\}$ NMR spectrum. Further,

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there is a simultaneous appearance of a new peak at δ 3.73 and 18.90 in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. The $^{195}Pt\{^1H\}$ NMR spectrum displays two peaks at δ −1885 and −1896. All these changes are consistent with the presence of a new species in solution, and the shifts are identical to those expected for the dinuclear complex β-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$. Further, a very pale-green/yellow solid precipitated from the solution after this time. This was identified as α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf by elemental analysis, ^1H NMR spectroscopy (in dmso-d_6), and molar conductivity. The color of the solution in the NMR tube also changes from pale amber to light yellow, which is consistent with this interpretation.

The ^1H NMR spectra of the dinuclear platinum(IV) complexes are almost identical to those observed for the platinum(II) analogues, and assignments of some of the resonances can be made on the basis of ^{195}Pt–^1H coupling constants. In the spectrum of α-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5H_2O$, the downfield signal at δ 13.91 is attributed to the dpzm N–H. The H-5 and H-3 ring protons can be assigned to the peaks at δ 8.26 and 7.77, respectively, as the latter possesses the larger ^{195}Pt–^1H coupling constant. These values are significantly smaller than those of the corresponding platinum(II) complexes and are a reflection of the larger s-contribution in dsp^2-hybridized platinum(II) in contrast to d^2sp^3-hybridized platinum(IV).[27] The signal at δ 3.91 is attributed to the methylene-bridge protons, and the broad signal at δ 3.55 is indicative of lattice water. The ^1H NMR spectrum of β-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5\text{dmf}\cdot0.5H_2O$ can be interpreted in a similar manner. The $^{13}C\{^1H\}$ NMR spectra of α-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5H_2O$ and β-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5\text{dmf}\cdot0.5H_2O$ are almost identical, and the assignments of the resonances are based on those of the corresponding platinum(II) complexes. No ^{195}Pt–^{13}C coupling is observed at 50.3 MHz.

In contrast to the similarity of the ^1H and $^{13}C\{^1H\}$ NMR spectra of α-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5H_2O$ and β-$[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]\cdot0.5\text{dmf}\cdot0.5H_2O$, the $^{195}Pt\{^1H\}$ NMR spectra display distinct singlets at δ +153 ($\Delta\nu_{1/2} \approx 53$ Hz) and δ +148 ($\Delta\nu_{1/2} \approx 46$ Hz), respectively. The small difference in chemical shift is consistent with the presence of distinct conformational isomers in solution. Further, comparisons between the α- and β-forms of $[Cl_4Pt(\mu\text{-dpzm})_2PtCl_4]$ are particularly interesting since a similar study cannot be made between the two forms of the corresponding $[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$ species owing to the low solubility of α-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot0.5$dmf in dmf.

The resonances of the ^1H NMR spectrum of *cis*-$[PtCl_4(\text{dmf})(\text{dpzmH})]Cl\cdot0.5$dmf can be assigned as described for the analogous platinum(II) species. The signals at δ 14.00 (N–H), 8.27 (H-5), 7.61 (H-3), and 4.09 (CH_2) are characteristic of a coordinated pyrazole-type moiety of dpzm. The additional peaks at δ 13.40 (N–H), 8.22 (H-3), and 8.20 (H-5) are attributed to the dangling, protonated pyrazole-moiety of the same ligand. No signal could be assigned to the protonated N-2 atom (which may be due to its broadness). The coordination of a dmf molecule to the platinum is consistent with the resonances at δ 8.17 (formyl H), 2.95 (CH_3), and 2.79 (CH_3) and in close agreement with the literature.[24] ^{195}Pt–^1H satellite signals are not observed for the dmf methyl resonances and coordination through the oxygen, rather than the nitrogen atom, is proposed. The position of the resonance at δ +15 in the $^{195}Pt\{^1H\}$ NMR spectrum of *cis*-$[PtCl_4(\text{dmf})(\text{dpzmH})]Cl\cdot0.5$dmf is anomalous. It might be expected that the substitution of a N-donor (dpzm) by an O-donor (dmf) ligand would shift the signal downfield. The spectroscopic changes observed for *cis*-$[PtCl_2(\text{dmf})(\text{dpzmH})]Cl$ in dmf solution over a period of several days were not apparent in the spectrum of the corresponding platinum(IV) complex. This is consistent with the general lower reactivity of platinum(IV) complexes toward substitution.[28]

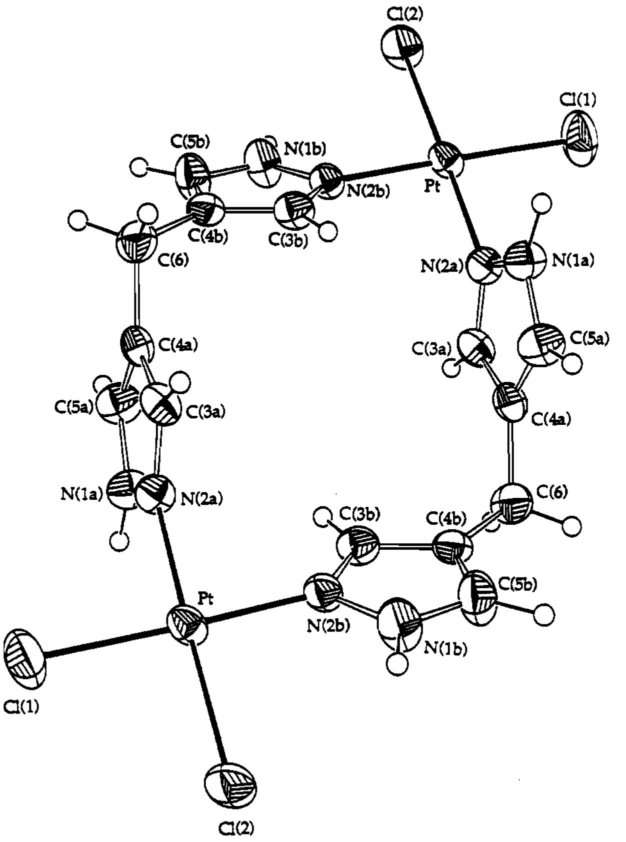

Figure 1. Molecular structure of γ-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]$. Thermal ellipsoids are represented at the 30% probability level.

Table III[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt	0.1666 (1)	0.2924 (1)	0.3094 (1)
Cl(1)	0.1410 (3)	0.1775 (2)	0.1661 (2)
Cl(2)	−0.0556 (3)	0.2587 (2)	0.3265 (3)
N(1a)	0.4491 (8)	0.2613 (6)	0.2655 (8)
N(2a)	0.3621 (7)	0.3265 (5)	0.2961 (6)
N(1b)	0.1369 (8)	0.4855 (5)	0.4163 (6)
N(2b)	0.1937 (7)	0.3943 (5)	0.4355 (6)
C(3a)	0.4288 (9)	0.4126 (6)	0.3072 (7)
C(4a)	0.5576 (9)	0.4038 (7)	0.2821 (7)
C(5a)	0.5635 (10)	0.3061 (7)	0.2558 (10)
C(3b)	0.2683 (9)	0.3932 (6)	0.5420 (7)
C(4b)	0.2601 (8)	0.4847 (6)	0.5926 (7)
C(5b)	0.1768 (10)	0.5399 (7)	0.5105 (8)
C(6)	0.6679 (9)	0.4837 (8)	0.2874 (7)
O	0.0071 (9)	0.4473 (5)	0.7999 (6)
N′	0.1774 (9)	0.4920 (7)	0.9595 (7)
C′	0.0757 (14)	0.5082 (9)	0.8708 (11)
MeC(1)	0.2274 (21)	0.3985 (15)	0.9852 (13)
MeC(2)	0.2508 (19)	0.5636 (16)	1.0357 (15)

[a] Estimated standard deviations are given in parentheses.

The $^{195}Pt\{^1H\}$ NMR spectrum of $[Cl_4Pt(\mu\text{-dpzm})_2PtCl_2]$ in particular provides conclusive evidence for the presence of mixed-oxidation states. The broad resonances centered at δ +154 and −1893 are consistent with platinum(IV) and platinum(II) centers, respectively, and with each having a *cis*-N_2Cl_2 type donor-atom environment. The mixed-oxidation state complex shows broad resonances in the region of the dpzm protons, which is unlike the sharp peaks found in the ^1H NMR spectra of the Pt(II)–Pt(II) or Pt(IV)–Pt(IV) complexes. The line broadening may perhaps be attributed to some form of electronic interchange between the metal centers as well as the presence of conformational isomers.

X-ray Crystal Structure. Suitable crystals were only obtainable for the γ-form. The crystal structure of the title complex consists of discrete molecules of complex separated by normal van der Waals contacts, and there is hydrogen-bonding to the dmf solvent. Figure 1 shows an ORTEP view of the complex with the atom-labeling scheme, and a stereoscopic drawing of the contents of one

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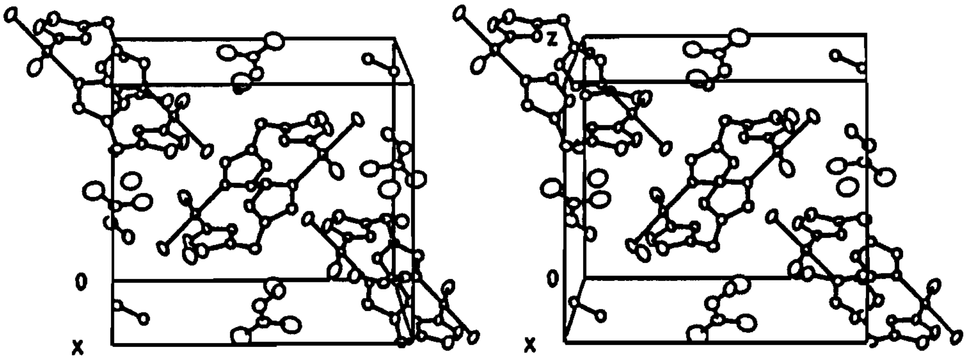

Figure 2. Stereoscopic packing diagram of γ-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·2dmf, showing the contents of one unit cell and the relative disposition of the dinuclear complex molecules. Hydrogen atoms have been omitted for clarity.

Table IV[a]

	Bond Lengths (Å)		
Pt–Cl(1)	2.292 (4)	N(1b)–C(5b)	1.32 (1)
Pt–Cl(2)	2.286 (4)	N(1b)–N(2b)	1.34 (1)
Pt–N(2a)	2.016 (8)	N(2b)–C(3b)	1.30 (1)
Pt–N(2b)	2.020 (7)	C(3b)–C(4b)	1.39 (1)
N(1a)–C(5a)	1.30 (1)	C(4b)–C(5b)	1.33 (1)
N(1a)–N(2a)	1.34 (1)	C(4b)–C(6)	1.50 (1)
N(2a)–C(3a)	1.32 (1)	O–C′	1.25 (1)
C(3a)–C(4a)	1.38 (1)	O–N′	2.27 (1)
C(4a)–C(5a)	1.36 (1)	N′–MeC(1)	1.35 (1)
C(4a)–C(6)	1.51 (1)	N′–MeC(2)	1.39 (2)
	Bond Angles (deg)		
N(2a)–Pt–N(2b)	88.6 (3)	C(3b)–N(2b)–N(1b)	106.1 (7)
N(2a)–Pt–Cl(1)	90.1 (2)	C(3b)–N(2b)–Pt	132.1 (6)
N(2b)–Pt–Cl(2)	89.8 (2)	N(1b)–N(2b)–Pt	121.7 (5)
Cl(2)–Pt–Cl(1)	91.4 (1)	N(2b)–C(3b)–C(4b)	110.3 (7)
C(5a)–N(1a)–N(2a)	110.5 (8)	C(5b)–C(4b)–C(3b)	105.0 (7)
C(3a)–N(2a)–N(1a)	105.5 (8)	C(5b)–C(4b)–C(6)	127.1 (8)
C(3a)–N(2a)–Pt	130.2 (6)	C(3b)–C(4b)–C(6)	127.9 (7)
N(1a)–N(2a)–Pt	124.2 (6)	N(1b)–C(5b)–C(4b)	108.5 (8)
N(2a)–C(3a)–C(4a)	111.0 (8)	C(4b)–C(6)–C(4a)	112.7 (8)
C(5a)–C(4a)–C(3a)	103.6 (8)	C′–N′–MeC(1)	120 (1)
C(5a)–C(4a)–C(6)	128.5 (9)	C′–N′–MeC(2)	126 (1)
C(3a)–C(4a)–C(6)	127.8 (8)	MeC(1)–N′–MeC(2)	113 (1)
N(1a)–C(5a)–C(4a)	109.4 (9)	O–C′–N′	129 (1)
C(5b)–N(1b)–N(2b)	110.1 (7)		

[a] Estimated standard deviations are given in parentheses.

unit cell is given in Figure 2. The atomic coordinates of non-hydrogen atoms are given in Table III, and bond geometries are presented in Table IV.

Each platinum atom of γ-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·2dmf is coordinated to two chlorine atoms in a cis configuration, with the remaining coordination sites occupied by the N-2 atoms of two bridging dpzm ligands. The arrangement of ligands about the platinum center is marginally distorted from an ideal square-planar geometry, and there are no significant deviations from or within the coordination plane. The two Pt–Cl distances (2.292 (4), 2.286 (4) Å) are in close agreement with the mean value of 2.293 (9) Å for a number of *cis*-[PtCl$_2$L$_2$] complexes (L = ligand with a sp^2-hybridized nitrogen-donor atom).[29] The two Pt–N bond lengths (2.016 (8), 2.020 (7) Å) are also in agreement with the average Pt–N distances for *cis*-[PtCl$_2$L$_2$] complexes (2.023 (12) Å).[29] The intramolecular distance between the two platinum atoms is 8.882 (1) Å.

The interatomic distances and angles of the pyrazole-type rings lie in the range of other platinum–pyrazole complexes,[20,30–43] and the atoms in each ring are essentially coplanar. Moreover, these parameters are comparable to those in all metal–pyrazole complexes which have been determined by X-ray crystallography as surveyed by Bonati.[44] Further, the internal/external bond angles obtained for γ-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·2dmf follow the empirical trends proposed by Bonati for coordinated pyrazoles in general. In summary, the size of the bond angle follows the order: C(3)–N(2)–M > N(1)–N(2)–M; N(2)–C(3)–C(4) > N(1)–C(5)–C(4); C(5)–N(1)–N(2) > C(3)–N(2)–N(1). The coordinated heterocyclic rings lie approximately perpendicular to one another (88.6 (3)°) and form angles of 77.38 (ring a) and 33.70° (ring b) with the plane of the platinum coordination sphere. The differences in interplanar angles may be attributed to a strong hydrogen bond (1.834 (7) Å) which exists between the N–H group of pyrazole-type ring b and the oxygen atom of the dmf of crystallization. A weaker interaction between the oxygen atom of dmf in an adjacent unit cell and the N–H group of the pyrazole-type ring a is also present (2.029 (8) Å). A weak intermolecular hydrogen bond between one chloride ligand and the N–H of the other ring a is also evident.

Since all the bond angles and distances calculated for γ-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·2dmf are within the expected ranges, it appears that the 16-membered ring system is not strained (cf. *cis*-[PtCl$_2$(Hpz)$_2$], where Hpz = pyrazole[20]). However, space-filling molecular models show that the pyrazole-type rings are very restricted in their movements. Each ring can only be completely rotated with great difficulty owing to steric hindrance by the adjacent pyrazole-type rings.

The recent X-ray structural elucidation of *cis*-[PtCl$_2$(Hpz)$_2$] is of interest here.[20] The molecular structure of this complex is essentially equivalent to the asymmetric unit of γ-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·2dmf, and both complexes share very similar bond angles and distances. Further, large differences in the angles between the planes of the pyrazole-type rings and the platinum square plane are also found in *cis*-[PtCl$_2$(Hpz)$_2$]. There is also a weak hydrogen-bonding interaction between the N–H group of one coordinated pyrazole-type ring and the chloride ligand of another molecule.

Discussion

The preparative scheme summarized in Scheme I leads to the isolation of two forms of the dinuclear platinum(II) complex [Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$] having different solubilities in dmf, which are designated α and β. The α-form is less soluble and has 0.5 molecules of dmf of crystallization, and the β-form, which is more soluble, has none. A third form of low solubility, γ, containing two molecules of dmf is obtained on recrystallization of the α-form

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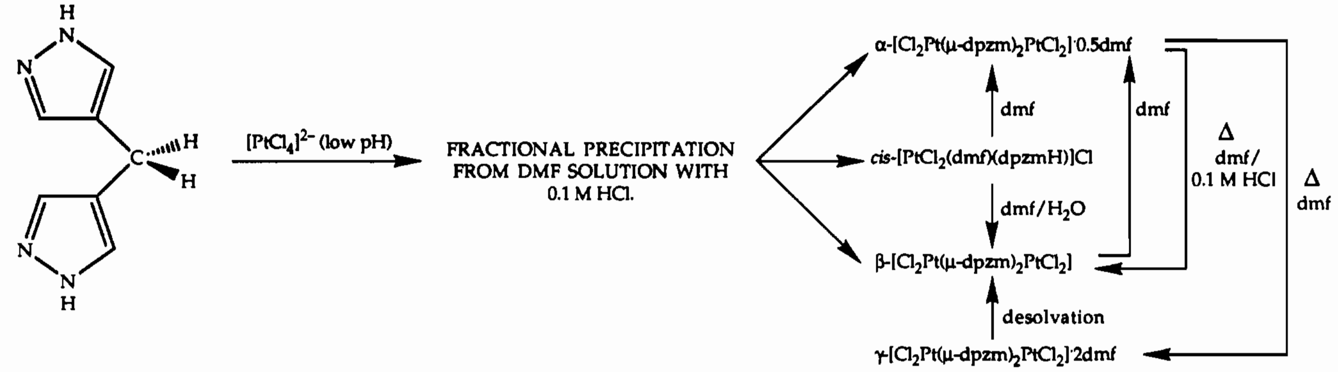
Scheme I. Synthesis of α-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·0.5dmf, β-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$], and *cis*-[PtCl$_2$(dmf)(dpzmH)]Cl from dpzm and [PtCl$_4$]$^{2-}$ at Low pH[a]



[a] See text for details.

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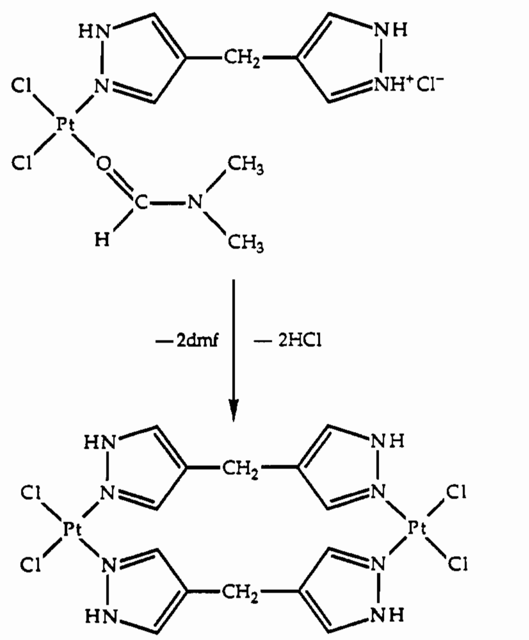

Figure 3. Dimerization of *cis*-[PtCl$_2$(dmf)(dpzmH)]Cl in dmf solution, which gives both α-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·0.5dmf and β-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]. The differences in the α- and β-complexes may be attributed to the orientation of the dpzm pyrazole-type rings relative to the platinum coordination plane.

from hot dmf. There are also distinctive color differences between the three forms. The α-form is a very pale-green/yellow, while the β-form is a pale yellow. The γ-form is obtained as clear, yellow diamond-shaped crystals. A mononuclear complex *cis*-[PtCl$_2$(dmf)(dpzmH)]Cl (Figure 3) is also obtained in which one end of the dpzm is protonated. This "dangling ligand" complex slowly dimerizes at room temperature to give a mixture of the α- and β-dinuclear complexes in dmf solution (Figure 3). In addition, and despite the change from square planar to octahedral geometry, a similar set of platinum(IV) dinuclear complexes, also differing in solvent(s) of crystallization, have been isolated together with the mixed-oxidation state complex [Cl$_4$Pt(μ-dpzm)$_2$PtCl$_2$].

A comparison of the "theoretical" X-ray powder diffraction pattern of γ-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·2dmf (calculated from single-crystal data) with the recorded powder patterns of the α- and β-forms shows them to be identical (Figure 4). Therefore, the presence of differing amounts of dmf of crystallization does not alter the powder pattern significantly, indicating that the crystal packing of the complex remains unchanged. This is commonly referred to as *crystal pseudopolymorphism*.[45] The introduction of dmf into the crystal lattice may have little effect in the X-ray powder patterns, where X-ray scattering is dominated by electron-dense atoms such as platinum and chlorine.

The exposure of γ-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·2dmf crystals to the atmosphere for a period of a few days at room temperature results in the loss of dmf of crystallization. This is accompanied by a breakdown of the crystals to give a pale-yellow powder, which has chemical and physical properties identical to those of β-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]. Provided that some unexpected conformational rearrangement of the pyrazole-type rings does not occur during the process of desolvation, then it is proposed that the molecular structure of the complex is *identical* in both β-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$] and γ-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·2dmf.

The α-, β-, and γ-forms of [Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$] can be interconverted as shown in Scheme I. The large dmf-solubility differences between the three forms can be attributed to differing amounts of lattice dmf, and may be the result of varying degrees of hydrogen-bonding between solvent and complex molecules. These differences cannot be due to crystal polymorphism (alternate packing arrangements of the same molecule in the crystal lattice), since the X-ray powder patterns are identical and hence crystal pseudopolymorphism is suggested.

Further discussion of the nature of the dinuclear complexes is complicated by the possible presence of conformational isomers. Although a consideration of molecular models shows that the 16-membered ring formed by the two metals and bridging ligands has some flexibility, the Pt–N bond rotation is restricted and up to five isomers may exist depending upon the orientations of N–H groups (Figure 5).

Proposed conformational differences between the α- and β-forms could explain the following observations. First, the mononuclear *cis*-[PtCl$_2$(dmf)(dpzmH)]Cl dimerizes in dmf over a period of a few days at room temperature to give approximately equal proportions of *both* α- and β-forms of the dinuclear complex (Figure 3). However, the addition of excess water to a dmf solution containing *cis*-[PtCl$_2$(dmf)(dpzmH)]Cl gives an immediate precipitate of β-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$], while the subsequent addition of excess 0.1 M HCl reprecipitates *cis*-[PtCl$_2$(dmf)(dpzmH)]Cl. Here, water deprotonates the dangling ligand, and the two molecules of the mononuclear species then react, with concomitant loss of coordinated dmf, to form the dinuclear complex. It is clear that in the mononuclear complex dpzm has freedom to rotate about the Pt–N bond and upon dimerization can give any of the five possible isomers. Second, a slow conversion of β-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$] to the thermodynamically favored α-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·0.5dmf in dmf solution is proposed, since addition of water to the dmf solution of *cis*-[PtCl$_2$(dmf)(dpzmH)]Cl results almost exclusively in the formation of β-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]. This is further supported by the observation that, over a period of a few months at room temperature, a sealed vessel containing a dmf solution of β-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$] deposits a very pale-green/yellow solid which has properties consistent with the α-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·0.5dmf formulation. Finally, the ^{1}H NMR spectrum of a 1:1 molar mixture of α-[Cl$_2$Pt(μ-dpzm)$_2$PtCl$_2$]·0.5dmf and β-[Cl$_2$Pt(μ-

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[45] Byrn, S. R. *Solid State Chemistry of Drugs*; Academic Press: New York, 1982; p 8.

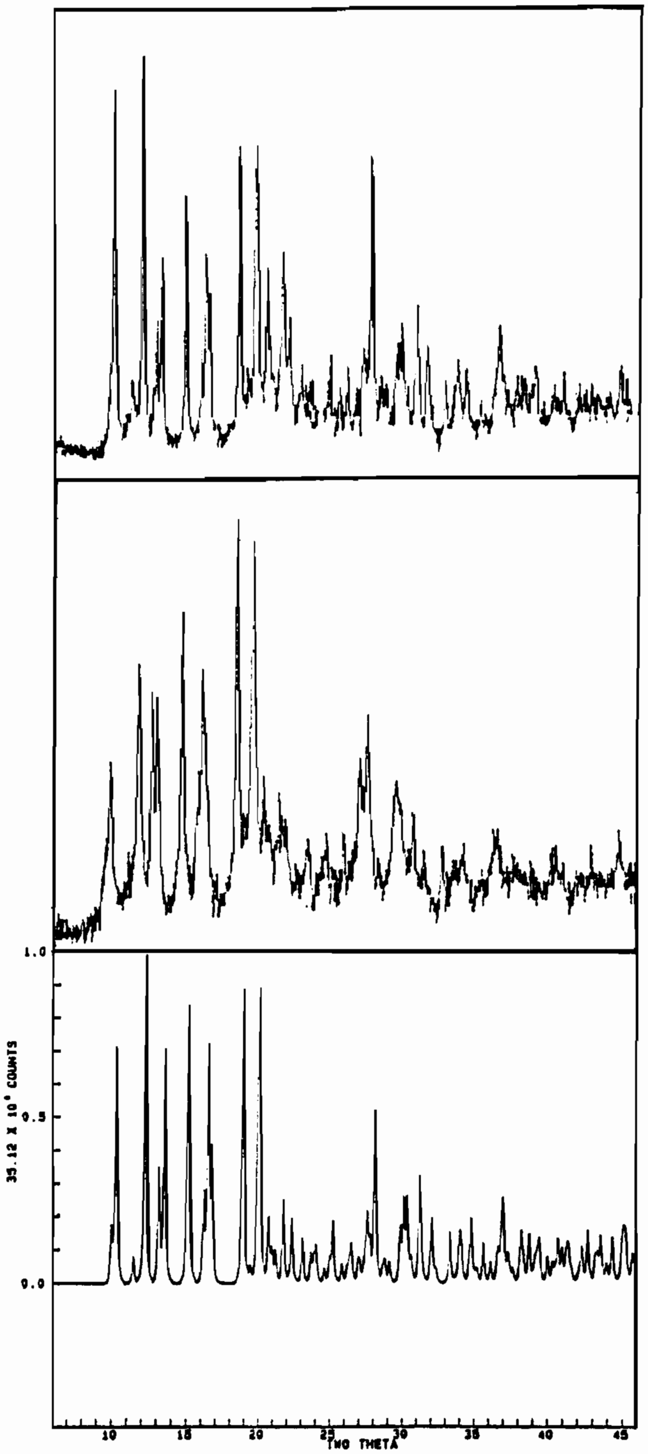

Figure 4. X-ray powder diffraction patterns of (from top to bottom) α-[$Cl_2Pt(\mu$-dpzm$)_2PtCl_2$]·0.5dmf, β-[$Cl_2Pt(\mu$-dpzm$)_2PtCl_2$], and γ-[$Cl_2Pt(\mu$-dpzm$)_2PtCl_2$]·2dmf. The powder pattern of the last mentioned is calculated from crystal data obtained from the single-crystal structure determination.

dpzm$)_2PtCl_2$] in dmso-d_6 shows distinct signals for the H-3 pyrazole-ring proton, and the $^{195}Pt\{^1H\}$ NMR spectra of α-[$Cl_4Pt(\mu$-dpzm$)_2PtCl_4$]·$0.5H_2O$ and β-[$Cl_4Pt(\mu$-dpzm$)_2PtCl_4$]·0.5dmf·$0.5H_2O$ in dmf-d_7 show distinct singlets at δ +153 and +148, respectively. The two NMR experiments therefore strongly support the proposal that the molecular structures of the α- and β-forms are not identical. At present the lack of suitable crystals has precluded studies other than for the 2-dmf solvate, but future ^{195}Pt NMR work using ^{15}N-enriched ligands should permit a closer identification of the various forms to be made.

It seems likely that one conformational isomer is present for [$Cl_2Pt(\mu$-Me_2dpzm$)_2PtCl_2$]·0.5dmf. Molecular models show that replacement of the N–H protons with methyl groups imposes a significant steric constraint on the movement of the bridging dpzm ligands, sufficient to prevent the interconversion of isomers.

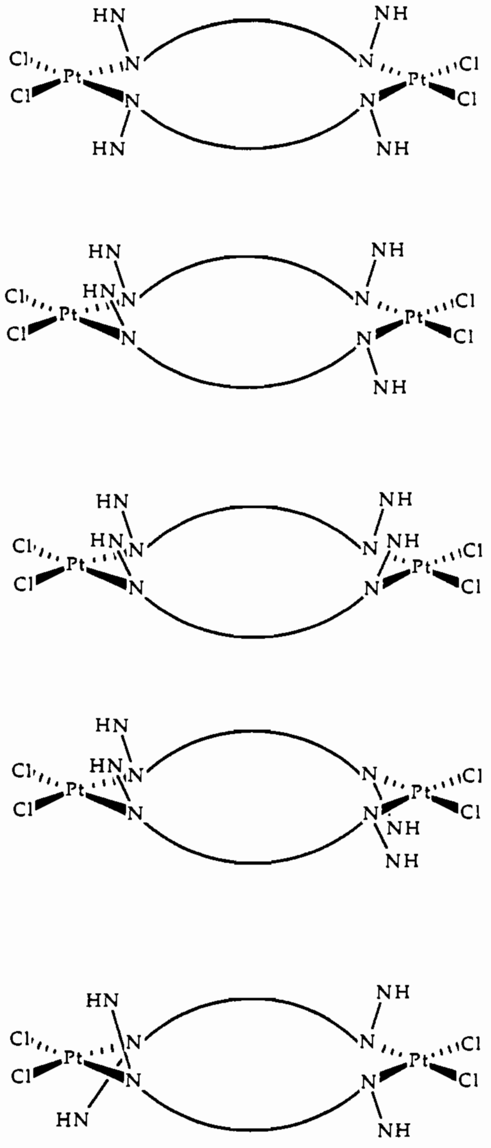

Figure 5. Possible conformational isomers of [$Cl_2Pt(\mu$-dpzm$)_2PtCl_2$]. The structure of the dpzm ligand is simplified for clarity.

Concluding Remarks

The formulations given for each of the new complexes are in agreement with the above physical measurements, as well as their chemical analyses. The molar conductivities correspond to nonelectrolytes for the dinuclear complexes. The low values (e.g. 8.4 and 12.4 S cm² mol⁻¹) found for the mononuclear complexes with protonated ligands may be explained by solvolysis and also by partial conversion when in solution to the dinuclear species, both of which are nonelectrolyte products.

The use of $K_2[PtCl_4]$ in neutral aqueous solution yields a pale green-yellow, amorphous solid which is insoluble in all common polar and nonpolar solvents. From its analysis and infrared spectrum it is likely that this is polymeric $[Pt(\mu\text{-dpzm})_2]_n[PtCl_4]_n$. The broad band at 325 cm^{-1} is attributed to $[PtCl_4]^{2-}$. A similar reaction with Hpz gives $[Pt(Hpz)_4][PtCl_4]$,[8] and the dpzm ligand and its derivatives are known to form polymeric complexes with other metals.[46,47] It is clear that polymer formation can be inhibited by lowering the concentration of free dpzm through the

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use of acid conditions as employed in this work.

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Supplementary Material Available: Tables of hydrogen atom positions, bond lengths/angles involving the hydrogen atoms, and anisotropic thermal parameters for γ-[$Cl_2Pt(\mu$-dpzm$)_2PtCl_2$]·2dmf and tables of assigned IR bands and X-ray powder diffraction *d*-spacings and relative intensities for the α-, β-, and γ-platinum(II) complexes (7 pages); a table of observed and calculated structure factors for γ-[$Cl_2Pt(\mu$-dpzm$)_2PtCl_2$]·2dmf (11 pages). Ordering information is given on any current masthead page.

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Exchange Interaction through a Croconato Bridge: Synthesis, Crystal Structure, and Magnetic Properties of (μ-Croconato)bis[{bis(2-pyridylcarbonyl)amido}copper(II)] Trihydrate

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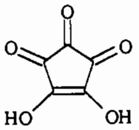
The title compound, denoted as $[Cu_2(bpca)_2(C_5O_5)]\cdot3H_2O$ (where bpca and $C_5O_5^{2-}$ are the bis(2-pyridylcarbonyl)amide anion, $C_{12}H_8N_3O_2^-$, and the dianion of 4,5-dihydroxy-4-cyclopentene-1,2,3-trione, respectively), has been synthesized, and its structure has been determined by X-ray crystallographic methods. Crystal data: monoclinic system, space group $P2_1/c$, $a = 19.535$ (2) Å, $b = 20.189$ (2) Å, $c = 7.5167$ (6) Å, $\beta = 97.485$ (8)°, $Z = 4$. Data up to $\theta = 26°$ (Mo Kα radiation) were collected at room temperature on a CAD-4 diffractometer. The structure was solved by a combination of Patterson and direct methods and refined by full-matrix least-squares refinement to conventional agreement indices $R = 0.063$ and $R_w = 0.080$ with 4341 observed reflections [$I \geq 3.0\sigma(I)$]. The structure consists of neutral croconato-bridged copper(II) dinuclear units and crystallization water molecules. The croconate acts as a bis-bidentate ligand bridging two crystallographically independent copper(II) ions separated by 6.824 (1) Å. The bis(2-pyridylcarbonyl)amido group is the end-cap ligand, and it is coordinated to copper(II) through its three nitrogen atoms. Each copper atom forms four short equatorial bonds to the three nitrogen atoms of bpca and one oxygen atom of croconate [1.927 (3)–2.003 (3) Å for Cu(1) and 1.934 (3)–1.997 (3) Å for Cu(2)] and a longer axial bond to an oxygen atom of the croconato bridge [2.585 (3) and 2.477 (3) Å for Cu(1) and Cu(2), respectively]. Cu(1) forms an additional axial bond and Cu(2) has an axial contact to an oxygen atom of respectively a croconato group [2.496 (3) Å] and a carbonyl group of a bpca ligand [2.932 (3) Å] from neighboring molecules. The magnetic behavior of this compound has been investigated in the 4.2–300 K temperature range, and it is as expected for an antiferromagnetically coupled copper(II) dimer with a singlet–triplet energy gap of 9.63 cm^{-1}. Variable-temperature X-band EPR spectra were also recorded. The exchange pathway is analyzed in the light of structural data and extended Hückel MO calculations. The ability of croconate to support a magnetic exchange interaction between two paramagnetic metal ions is compared to that of the related oxalato, squarato, and hydranilato bridges.

Introduction

The dianion of 4,5-dihydroxy-4-cyclopentene-1,2,3-trione (**1**), $C_5O_5^{2-}$, commonly referred to as the croconate anion, is a member



$H_2C_5O_5$

1

of the so-called monocyclic oxocarbon dianions [n = 3 (deltate), 4 (squarate), 5 (croconate), 6 (rhodizonate)] to which considerable attention has been devoted during the last years.[2-4] However, much work remains to be done in order to fully characterize the coordination chemistry of these polyatomic molecules. So, although the first synthesis of deltic acid was reported by West and Eggerding[5] in 1975, its coordinating capability remains unknown. The squarate ligand is the best known of this series. In a recent paper some of us focused on it and characterized structurally its bonding properties to copper(II) ion.[6] Crystal structures of squarate-containing copper(II),[6,7] zinc(II),[8] nickel(II),[9] manganese(II),[8b] chromium(III),[10] iron(III),[11] polyoxomolybdate,[12]

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