Metal–Metal Interactions in Linear Chains. The Structure and Characterization of Bis(pyridine-2-carboxaldoximinato)platinum(II) Dihydrate

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Abstract: The crystal structure of bis(pyridine-2-carboxaldoximinato)platinum(II) dihydrate, $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$, has been determined from three-dimensional x-ray data obtained using an automatic four-circle diffractometer and Mo Kα radiation. The material crystallizes in the space group *Ibam* of the orthorhombic system with four formula units in a cell of dimensions a = 11.378 (5), b = 18.561 (6), and c = 6.490 (2) Å. The observed and calculated densities are 2.27 (2) and 2.29 g cm^{-3}, respectively. The structure has been refined by full-matrix least-squares methods using 853 independent intensities to a final value of the conventional R factor (on F) of 0.031. The structure consists of linear chains of planar $[Pt(C_6H_5N_2O)_2]$ units which are hydrogen bonded through the ligand oxygen atom to water molecules. The coordination around the platinum centers is roughly square planar, the ligating atoms being the two nitrogen atoms from each of two ligands. The planar units form a chain parallel to the crystallographic c axis, with a Pt–Pt separation of 3.245 (1) Å ($c/2$). The ligands in adjacent molecules in the chain are rotated relative to each other so that there is no overlap between the pyridine rings. A powdered sample of the complex shows enhanced electrical conductivity which is in the same range as that observed for Magnus' Green salt.

The chemical and physical properties of directly interacting transition metal ions in metal complexes have received considerable recent attention.[1] One of the major reasons for this interest is the suggestion that complexes which involve chains of metal ions coordinated to highly polarizable ligands have considerable potential as superconductors.[2] Square planar complexes which stack in this manner, however, have been found to vary in their electrical properties from electrical insulators (e.g., $K_2[PtCl_4]$)[3] to the highly conducting mixed-valence complex $K_2[Pt(CN)_4Br_{0.3}]\cdot 3.2H_2O$ (KCP), whose exact formulation is still under investigation.[4,5] Unfortunately, KCP apparently undergoes a Peierls transition at very low temperatures[6] which renders it unsuitable for superconductivity.

A large number of related square planar d^8 complexes also forms stacked materials, but all suffer from the disadvantage that they are not susceptible to facile chemical modification of the ligands and are not, therefore, useful for the study of the effects of subtle changes in the electronic environment at the metal centers. The reports of the synthesis[7] and spectral properties of bis(pyridine-2-carboxaldoximinato)platinum(II), however, allowed us to overcome this drawback, since the ligand contains some chemical functionality which can be used to bring about the desired small changes at the metal. Hence, we have undertaken a systematic structural and conductometric study of this complex and its derivatives; we report here the structure and conductivity properties of the parent complex, bis(pyridine-2-carboxaldoximinato)platinum(II) dihydrate.

Experimental Section

Synthesis. The complex was prepared by a modification of the method of Krause and Busch,[7] and recrystallized from hot chloroform solution. Blood-red crystals suitable for x-ray crystallography (vide infra) were obtained by slow cooling of a chloroform solution of the complex.

Spectra. Infrared spectra were measured in KBr disks on a Digilab FTS-14 spectrometer using a resolution of 2 cm^{-1} and are believed to be accurate to 2 cm^{-1}. Electronic spectra were measured on a Cary 17 for solution and mull techniques, while a Unicam SP-1800 was used to measure the visible region of a KBr disk sample. Diffuse reflectance spectra were measured by grinding a sample of the complex in mineral oil and spreading the sample on Whatman no. 1 filter paper. A piece of oiled filter paper was placed in the reference beam. A finely ground sample of the complex in a KBr pressed disk was also measured in the visible region. ^{1}H NMR spectra were measured in $CDCl_3$ on a Varian XL-100 spectrometer using Me_4Si as an internal reference.

Conductivity. Samples for electrical conductivity were made by pressing a finely or sparingly ground sample of the complex in a Perkin-Elmer stainless steel die using 14 000–22 000 lb force. The fragile pellets were then placed between spring loaded platinum contacts and the ac conductivity was measured using the three-probe method[9] with a General Radio capacitance bridge and tuned amplifier and null detector.

Collection and Reduction of the X-Ray Data. A crystal measuring 0.005 × 0.004 × 0.056 cm in the [1 10], [010], and [001] directions was used for space group assignment and intensity data collection. Weissenberg and precession photographs taken with Cu Kα and Mo Kα radiations indicated systematic absences of $h + k + l$ odd for hkl, k odd for $0kl$, and h odd for $h0l$ reflections which would indicate either space groups *Ibam* ($D_{2h}{}^{26}$) or *Iba2* ($C_{2v}{}^{21}$) of the orthorhombic system. The cell constants and their standard deviations, determined by the least-squares procedure of Busing and Levy[10] on 12 carefully centered reflections, are a = 11.378 (5), b = 18.561 (6), and c = 6.490 (2) Å. The measured density of the crystal by flotation in a mixture of bromoform and benzene is 2.27 (2) g cm^{-3} and the calculated density assuming four molecules per unit cell is 2.29 g cm^{-3}. Hence, the molecules are required to lie in special positions in the unit cell (vide infra).

The crystal was mounted on a glass fiber parallel to the c axis, and in this orientation intensity data were taken at a takeoff angle of 2.0°; at this angle the peak intensity of a typical strong reflection was approximately 90% of the maximum value as a function of takeoff angle. A total of 1232 independent reflections was examined using Mo Kα by the θ–2θ scan technique in the range $2° \leq 2\theta(\text{Mo K}\alpha) \leq 60°$ at a scan rate of 1.0° min^{-1}. To allow for the presence of both Kα_1 and Kα_2 radiations, the scan range for each reflection was from 0.95° below the calculated Kα_1 peak position to 0.95° above the calculated Kα_2 position. Stationary-counter, stationary-crystal background counts of 10 s were taken at each end of the scan.

The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω-scan technique and was judged to be acceptable, with an average peak width at half-height of 0.16°. Throughout the data collection the intensities of three reference reflections were measured after every 100 reflections. All three reference reflections showed approximately an 8% decline in intensity during the run, and a linear correction was applied to account for this observed loss in intensity as a function of x-ray exposure.[11]

Data processing was carried out as described by Corfield et al.[12]

Table I. Positional Parameters ($\times 10^4$) for $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$

Atom	X	Y	Z
Pt	0	0	0
N(1)	688 (7)	1003 (4)	0
C(1)	1856 (11)	1031 (7)	0
C(2)	2471 (11)	1674 (7)	0
C(3)	1848 (12)	2304 (6)	0
C(4)	668 (12)	2279 (5)	0
C(5)	126 (12)	1617 (5)	0
C(6)	2432 (9)	326 (7)	0
N(2)	1736 (8)	−223 (4)	0
O(1)	2183 (7)	−865 (5)	0
O(2)	4567 (12)	−922 (9)	631 (54)
HC(2)	3312	1677	0
HC(3)	2243	2754	0
HC(4)	213	2713	0
HC(5)	−693	1604	0
HC(6)	3262	274	0
HO(2)[a]	3700	−900	500

[a] This atom, which is associated with the water oxygen O(2), was not included in the refinement; see text for discussion.

Table II. Thermal Parameters (in Å^2) for $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$[a]

Atom	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	32 (0)	30 (0)	24 (0)	−1 (1)	0	0
N(1)	44 (4)	35 (3)	25 (3)	−6 (3)	0	0
C(1)	36 (6)	48 (6)	52 (7)	−5 (5)	0	0
C(2)	61 (7)	54 (6)	72 (9)	−21 (6)	0	0
C(3)	65 (7)	47 (6)	62 (9)	−15 (5)	0	0
C(4)	66 (7)	32 (4)	63 (8)	−6 (4)	0	0
C(5)	43 (7)	32 (3)	57 (6)	−4 (4)	0	0
C(6)	29 (4)	58 (6)	49 (7)	−3 (4)	0	0
N(2)	45 (5)	42 (3)	45 (5)	0 (3)	0	0
O(1)	35 (4)	40 (4)	68 (6)	6 (3)	0	0
O(2)	53 (5)	99 (10)	181 (52)	9 (6)	3 (11)	11 (16)
HC(2)	63					
HC(3)	63					
HC(4)	63					
HC(5)	63					
HC(6)	63					

[a] Anisotropic thermal parameters are $\times 10^3$. Isotropic thermal parameters are $\times 10^3$. The form of the anisotropic thermal parameters is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

After correction for background the intensities were assigned standard deviations according to the formula $\sigma(I) = [C + 0.25(ts/tb)^2(B_H + B_L) + p^2I^2]^{1/2}$ where the symbols have their usual meanings and the value of p was chosen as 0.04. The last term in this equation is an empirical term which raises the standard deviation of very intense reflections and allows for systematic errors in these intensities. The intensities and their standard deviations were corrected for Lorentz-polarization effects and for absorption.[13] The absorption coefficient of this compound for Mo Kα radiation is 114.24 cm^{-1}, and for the sample chosen transmission coefficients were found to range from 0.39 to 0.55. Of the 1232 reflections collected, 853 with $F^2 > 3\sigma(F^2)$ were considered observed after 12 low-order reflections were rejected because their peak profiles were sufficiently asymmetric to preclude a linear background correction, and only these observed reflections were used in subsequent calculations. Of these 853 observed intensities, only 35 had l odd. This abnormal intensity distribution is due to the special position of the platinum (vide infra), which requires that the heavy atom not contribute to l odd reflections in space group *Ibam*.

Solution and Refinement of the Structure. The solution of the structure was initiated assuming the centrosymmetric space group, *Ibam*. In this space group with four molecules in the unit cell the platinum atom must lie on a special position with either $2/m(C_{2h})$ or $222(D_2)$ symmetry and the ligands must also be in one of three symmetry-restricted environments having either a twofold rotation, a mirror plane, or an inversion center; in the absence of disorder, only the mirror plane is possible for this ligand. The platinum atom was positioned at (0,0,0) ($2/m$) and the ligand atoms were located in the $(x,y,0)$ mirror plane. The conventional R factor (vide infra) on the platinum atom alone was 0.12 and subsequent difference Fourier maps phased only on the platinum atom revealed the x,y coordinates of all remaining nonhydrogen atoms.

All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factor for Pt was taken from Cromer and Waber,[14] that for H from Stewart, Davidson, and Simpson,[15] and those for C, O, and N were from Ibers.[16] The effects of the anomalous dispersion of platinum were included in all calculations of F_c,[17] the values of $\Delta f'$ and $\Delta f''$ for Pt being taken from the tabulation of Cromer.[18] The unweighted and weighted residuals are defined as

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| \text{ and}$$
$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$$

A difference Fourier map based on anisotropic refinement of all 11 nonhydrogen atoms contained electron density in positions which could be attributed to the ring hydrogen atoms. These atoms were, therefore, included in subsequent least-squares calculations, their positions being calculated on the basis of planar geometry in the ring and C-H distances of 0.95 Å; each hydrogen atom was assigned an isotropic thermal parameter of 5.0 Å^2, and no hydrogen atom parameter was varied. The hydrogen atoms associated with the water molecule could not be located with any certainty, presumably as a result of the large thermal vibration of the water oxygen atom, and were omitted from the refinement.

Examination of the thermal parameters U_{ij} of the water oxygen atom showed that U_{33}, i.e., the amplitude of vibration parallel to the chain direction, was very large. Consequently, we decided to allow the water molecule to occupy a $^{50}/_{50}$ disordered position above and below the molecular ($xy0$) plane. The change had very little effect on R_2, but the disordered model led to a much more reasonable model for the thermal motion of this atom.

In the final cycle of refinement there were 68 varied parameters including the scale factor and 853 reflections which gives a reflection to parameter ratio of 13:1. In the last least-squares cycle no parameter shifted by more than 0.10 esd which indicated that refinement had converged. The final R_1 and R_2 values were found to be 0.031 and 0.034, and the error on an observation of unit weight was observed to be 0.95. The value of R_2 showed no dependence on $\sin\theta$ or on $|F_o|$, which indicates that our assignment of $p = 0.04$ in the weighing scheme is essentially correct. Examination of the final values of $|F_o|$ and $|F_c|$ suggested that no correction for extinction is appropriate.

A final difference Fourier map showed no peak above 0.7 eÅ^{-3} except for some residual density of height 1.2 eÅ^{-3} near the platinum atom. This residual density is presumably due to some small error in our absorption correction, and is not wholly unexpected in view of the large value of μ_a of platinum for this radiation. The probable location of one of the water hydrogen atoms was obtained from this map, but this atom was not included in any refinement; the second hydrogen atom of the water moleculer could not be located.

The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A table of observed and calculated structure amplitudes is available.[19]

Description of the Structure

The structure consists of chains of stacked $Pt(C_6H_5N_2O)_2$ molecules separated along the crystallographic c axis (or Pt-Pt axis) by 3.245 (1) Å. The coordination sphere around the Pt atom is required by the space group to exhibit $2/m$ symmetry; hence, all the atoms in the molecule are constrained to lie in a mirror plane. A view of this unit is given in Figure 1.

The two independent Pt-N bond distances are 2.019 (9) and 2.021 (7) Å, which are similar to Pt-N distances found by other workers.[20,21] No unusual distances or angles were found in the pyridine ring.

The C(6)-N(2) distance is 1.29 (1) Å which is in the range of accepted carbon-nitrogen double bonds[22] and the

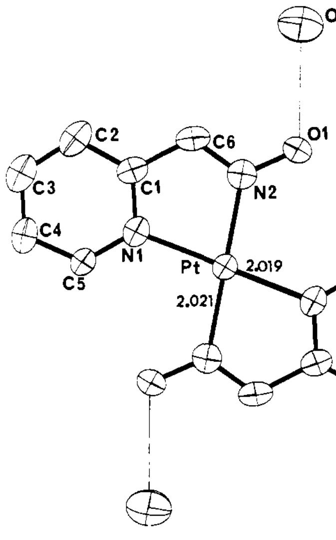

Figure 1. A single formula unit of $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$ viewed along the crystallographic *c* axis. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

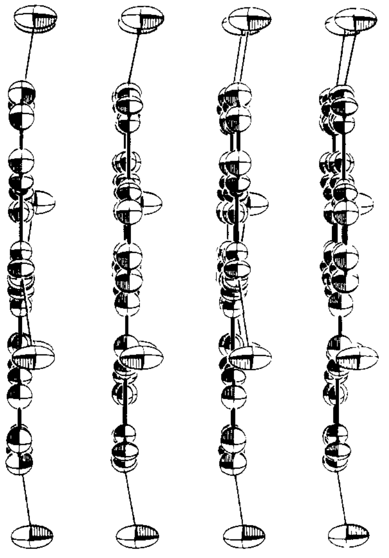

Figure 2. The stacking arrangement in the crystals of $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$ as viewed normal to the crystallographic *c* axis. Only one of the two disordered water positions is shown.

N(2)-O(1) distance of 1.29 (1) would seem to be an appropriate distance for a nitrogen-oxygen single bond.[22] The N(1)-Pt-N(2) and N(1)-Pt-N(1)′ angles are 79.1 (3) and 100.9 (3)°, respectively. Angles about the C(6) and N(2) atoms are 115.6 (10) and 115.9 (7)°, respectively, which are values that would be expected for sp^2 type atoms. All pertinent bond distances and angles and their standard deviations are listed on Table III.

This complex crystallizes with a molecule of water per ligand molecule and a resulting oxygen-oxygen distance of 2.75 (1) Å between O(1)-O(2) is observed. This short O(1)-O(2) distance strongly suggests that there is a hydrogen bond between the ligand oxygen atom and the water molecule; such an interaction is not surprising in view of the formal negative charge on O(1). The hydrogen atom which was located in the final difference Fourier map lies at a distance of 1.76 Å from the oxime oxygen atom, and the resulting O-H···O angle is 169°. While this hydrogen atom was not refined, these data suggest a strong O-H···O hydrogen bond. This O···O separation is, however, longer than the values of 2.52-2.62 Å reported for Ni, Cu, and Pd salicylaldoxime complexes.[23-26]

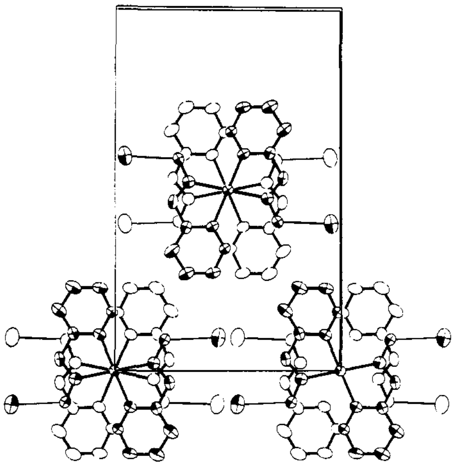

Figure 3. The columns of $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$ molecules viewed down the crystallographic *c* axis. The cross-hatched atoms lie *c*/2 (3.245 Å) above the open atoms. This view shows the lack of overlap between pyridine rings in the columns.

Table III. Selected Interatomic Distances (Å) and Angles (deg) in $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$

Distances		Angles	
Pt(1)-N(1)	2.019 (9)	N(1)-Pt(1)-N(2)	79.1 (3)
Pt(1)-N(2)	2.021 (7)	C(1)-N(1)-Pt(1)	115.0 (8)
N(1)-C(1)	1.33 (1)	C(1)-N(1)-C(5)	127.9 (8)
C(1)-C(2)	1.38 (2)	N(1)-C(1)-C(6)	114.5 (11)
C(2)-C(3)	1.37 (2)	N(1)-C(1)-C(2)	122.6 (12)
C(3)-C(4)	1.34 (2)	C(1)-C(2)-C(3)	118.4 (11)
C(4)-C(5)	1.37 (1)	C(2)-C(3)-C(4)	119.2 (11)
C(5)-N(1)	1.31 (1)	C(3)-C(4)-C(5)	118.7 (12)
C(1)-C(6)	1.46 (2)	C(6)-C(5)-N(1)	124.1 (13)
C(6)-N(2)	1.29 (1)	C(1)-C(6)-N(2)	115.6 (10)
N(2)-O(1)	1.29 (1)	C(6)-N(2)-O(2)	119.1 (10)
O(1)-O(2)	2.75 (1)	Pt(1)-N(2)-O(2)	125.0 (7)
O(2)-H(6)	1.0	O(1)-H(6)-O(2)	169

The overall packing in the crystal is depicted in Figures 2 and 3. In Figure 2 a view parallel to the *a* axis shows the stacking phenomenon observed in this structure and the position of one of the disordered oxygen atoms; the other, which would, of course, be located across the mirror plane (*xy*0), is omitted. Figure 3 is a view down the *c* axis (or metal-metal axis) and shows very clearly how the ligands chose to utilize the maximum amount of space to, as far as possible, avoid overlap with molecules above or below in the stacking arrangement. Hence, as is seen in Figure 3, there is an almost complete absence of overlap of neighboring ring systems; necessarily, however, extracyclic chains of the ligands retain approximately the interlayer separation for their van der Waals' distances.

Discussion

The ir spectra in Nujol of the Pt complex show bands attributable to hydrogen bonded OH at 3180 and 1652 cm^{-1}; these bands are presumably due to the water of crystallization. Several of the major ligand bands shift or disappear. The C=N or C—C stretch ligand band near 1590 cm^{-1} shifts to 1617 cm^{-1} upon complexation, indicating strong interaction of the Pt with the heterocyclic ring. The strongest ligand band at 985 cm^{-1} is not present in the platinum complex. These spectral results are entirely consistent with the crystallographic findings (vide supra).

The uv-visible spectrum of the complex was measured in the solid state and in solution. The solution spectrum is characterized by intense charge transfer or intraligand transitions (see Table IV). The solid-state spectrum is less

Table IV. Electronic Spectra for $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$ and $C_6H_6N_2O$

Compound	Absorption maxima (nm)
Free ligand[a]	207, 246, 273, 278, 287 sh
$[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$[b]	258 sh, 266, 301, 330 sh, 348, 384, 422 sh, 439, 459
$[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$[c]	<350, 436, 508

[a] 95% ethanol. [b] Dichloromethane. [c] KBr.

Table V. Frequency Dependence of the Conductivity of $[Pt(C_6H_5N_2O)_2]\cdot 2H_2O$

Frequency, kHz	Conductivity, Ω^{-1} cm^{-1} (x10^9)[a]
5	1.2, 1.8
10	1.7, 3.02
20	2.25, 5.05

[a] The two values reported for each frequency were obtained from two different samples.

well resolved than the solution but is similar to the solution spectrum except for the presence of a distinct shoulder at 508 nm which is not present in solution spectra. This shoulder is present using both Nujol and KBr disks. Similar low energy bands are commonly found in other planar molecules which stack;[27] these bands have been assigned as perturbed single ion or molecule bands.[28]

The ^1H NMR spectra of the free ligand and of the complex in $CDCl_3$ show that, while the β and γ protons of the pyridine moiety are not greatly shifted by the complexation, the α proton and the imine proton undergo considerable shifts. The imine proton shifts upfield from δ 8.17 to 7.91 on complexation, and is coupled to the platinum nucleus with $^3J = 55$ Hz; the α proton is shifted downfield from δ 8.53 to 10.28, and is coupled to the Pt with $^3J = 38$ Hz.

Electrical conductivity measurements on pressed pellets (Table V) show that the conductivity of approximately 2×10^{-9} Ω^{-1} cm^{-1} is comparable to that reported[29] for $[Ir(CO)_2acac]$, which also forms a linear chain structure in the solid state[30] with an Ir-Ir separation of 3.20 Å. By comparison the corresponding yellow Pd complex has a conductivity of 1.9×10^{-13} Ω^{-1} cm^{-1}, which suggests that there is little or no interaction between the metal atoms. The conductivity of this platinum complex is also greater than that of the recently reported palladium bis(1,2-benzoquinondioximato) complex[31] and is comparable to the values of 2.0×10^{-8} and 2.1×10^{-9} Ω^{-1} cm^{-1} reported for pressed pellets of Magnus' Green salt, $[Pt(NH_3)_4][PtCl_4]$.[3,32] These conductivity values must be regarded as lower limits; thus, in related Pt and Ni complexes the anisotropic conductivity along the metal-metal direction as measured on a single crystal has been shown to exceed that of the pellet sample by a factor of 10^4 or 10^5.[3] Unfortunately, we have not yet succeeded in growing a single crystal of this complex which is suitable for such anisotropic measurements.

Since the crystal structure analysis shows that there is minimal overlap between the π-systems of the pyridine rings in neighboring complexes in the chains, it is apparent that the enhanced conductivity observed for this system cannot be due to the π-π overlap which has been suggested for other complexes[33] and is, therefore, attributable to the direct overlap of the metal orbitals.

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Supplementary Material Available. A listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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