moments of ferric dithiocarbamates are *lowered* by doping them into the cobalt(III) analogues that were isostructural between the two metals. The effect of doping the Fe(dtc)$_3$ into the low-spin Co(dtc)$_3$ crystal is analogous to an applied external pressure of hundreds of atmospheres.[25] We observed a greater relative intensity of the peaks assigned to the $^6A_1$ state in the In(III) matrix compared to the Co(III) matrix (cf., low-temperature spectra in Figure 1c). The previous dithiocarbamate results[20,25] support our present work.

The EPR spectra of Fe(SSeCN(C$_2$H$_5$)$_2$)$_3$ indicate changes in the strength of the ligand field, and indeed, there is no evidence of significant intermolecular interaction between neighboring Fe(III) atoms in the undiluted system.

The comparison of the solid magnetic moments in Table I reveals that, for these diethyl complexes in the solid state, the expected ligand-field strength increases with increasing size of chalcogen: $^-\mathrm{OSCNR_2} < {}^-\mathrm{S_2CNR_2} < {}^-\mathrm{SSeCNR_2} < {}^-\mathrm{Se_2CNR_2}$ is not uniformly observed; $^-\mathrm{S_2CNEt_2} > {}^-\mathrm{SSeCNEt_2}$ at room temperature; $^-\mathrm{S_2CNEt_2} > {}^-\mathrm{SSeCNEt_2} > {}^-\mathrm{Se_2CNEt_2}$ at 90 K. Also noteworthy is the anomalously low magnetic moment for Fe(Et$_2$dsc)$_3$ at temperatures below 20 K. Similar low-temperature results have been reported for Fe(OSCNEt$_2$)$_3$[8] and were ascribed to weak antiferromagnetic interactions. An alternative explanation involves the presence of diamagnetic impurities. Magnetic susceptibility studies are now in progress on other thioseleno- and diselenocarbamates of iron(III) derivatives to examine this trend.

The comparison of g values in Table II reveals no significant changes in g values for Fe(III) in going from a Co(III) to In(III) matrix, but does support earlier reports[18] of g values for the narrow line in the $g = 2$ region increasing: $^-\mathrm{SSeCNR_2} < {}^-\mathrm{Se_2CNR_2}$.

These results, combined with an earlier study[18] on undiluted complexes, indicate clearly that the thioselenocarbamates and diselenocarbamates of Fe(III), like the dithiocarbamates of Fe(III),[4–6] are in spin-state equilibrium, involving two distinct electronic states.

Acknowledgment. We wish to acknowledge the assistance of Dan Patterson in obtaining preliminary EPR spectra and T. Thanyasiri for his help in measuring the solid magnetic moments. W.D. wishes to express his appreciation to the Center for International and Comparative Programs, Kent State University, for support. Support from NSF Grant CHE83-00516 is gratefully acknowledged.

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Solid-State Emission of Dicyanoplatinum(II) and -palladium(II) Complexes of Substituted 2,2′-Bipyridines and 1,10-Phenanthroline and X-ray Crystal Structures of Isomorphous M(bpy)(CN)$_2$ (bpy = 2,2′-Bipyridine; M = Pt, Pd)

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Received September 29, 1988

Square-planar metal d^8 complexes are known to exhibit metal–metal bonding interactions in the solid state.[2] Such interactions between molecules stacked within a chain lead to anisotropic and characteristic spectral properties. In the course of designing new catalysts for photochemical substrate reduction and oxidation, we become interested in square-planar platinum(II) complexes having planar and nonbulky π-acid ligands such as 2,2′-bipyridine, cyanide, and alkyl isocyanides. Platinum(II) complexes of this type are likely to have long-lived excited ($d_{\sigma}{}^{*}p_{\sigma}$) triplets, which are emissive as suggested by the studies of Gray and co-workers.[3] We report here solid-state emission properties of a class of Pt(L-L)(CN)$_2$ compounds (L-L represents a chelating aromatic diamine) that are stacked and columnar as illustrated by the X-ray structure of Pt(bpy)(CN)$_2$ (bpy = 2,2′-bipyridine).[4] The X-ray structure of Pd(bpy)(CN)$_2$ and its spectroscopic properties are also included for comparison.

Experimental Section

Reagents and Chemicals. K$_2$PtCl$_4$ and Pd(CN)$_2$ were purchased from Strem. The ligands 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 4,4′-dimethyl-2,2′-bipyridine (4,4′-Me$_2$bpy) were obtained from Aldrich. Pt(CN)$_2$·xH$_2$O was prepared by literature methods.[5,6]

Instruments. Steady-state emission spectra (corrected) were recorded with Corning filters on a Hitachi 650-60 fluorescence spectrophotometer. Solid-state emission lifetimes were measured with a Quanta-Ray Q-switched DCR-3 pulsed Nd:YAG laser (excitation 355 nm).

Pt(bpy)(CN)$_2$. The complex was prepared by the following two methods.

Method A. A mixture of Pt(CN)$_2$·xH$_2$O (0.5 mmol) and 2,2′-bipyridine (3 mmol) in pyridine (15 mL) was stirred and refluxed for 20 h. An orange-red suspension was obtained. Upon cooling of the solution to room temperature and addition of diethyl ether, an orange-red solid precipitated out, which was filtered out and washed with diethyl ether. The yield was 52%.

Method B. Pt(CN)$_2$·xH$_2$O (1 mmol) was dissolved in aqueous ammonia (20%, 20 mL), which was then added dropwise to a refluxing dimethylformamide solution of 2,2′-bipyridine (9 mmol in 20 mL). After addition, the solution was refluxed for 5 h, during which the color changed from yellowish green to orange and then red. After refluxing, the solution mixture was cooled to 0 °C. An orange-red solid was deposited, which was filtered out and washed with ice-cooled dimethylformamide and diethyl ether. The yield was 63%. The crude product was then recrystallized in hot dimethylformamide (0.3 g in 200 mL) to give red needle-shaped crystals.

Both methods gave the same product as judged by their identical UV–vis spectra in dimethylformamide.

Anal. Calcd for Pt(bpy)(CN)$_2$: C, 35.7; H, 2.0; N, 13.9. Found: C, 35.5; H, 2.3; N, 14.1. IR (Nujol mull): ν(CN), 2130, 2120 cm^{-1}.

Pt(4,4′-Me$_2$bpy)(CN)$_2$·2H$_2$O. Pt(CN)$_2$·xH$_2$O (2.4 mmol) was dissolved in aqueous ammonia (25%, 50 mL), which was added dropwise to a refluxing dimethylformamide solution of 4,4′-Me$_2$bpy (24 mmol in 70 mL). The solution was heated at 100 °C for 7 h. Upon cooling of the solution, a yellow solid together with the white free ligand was deposited. The free ligand was separated from the product by washing with dichloromethane. The crude product was yellowish green in color and was purified by recrystallization in hot acetonitrile. The yield was 60%.

Anal. Calcd for Pt(4,4′-Me$_2$bpy)(CN)$_2$·2H$_2$O: C, 36.0; H, 3.5; N, 12.0. Found: C, 35.7; H, 3.1; N, 12.0. IR: ν(OH), 3400 cm^{-1} ν(CN), 2130, 2120 cm^{-1}.

Pt(phen)(CN)$_2$. It is similarly prepared as its bpy analogue. The crude product was recrystallized in hot dimethylformamide to give violet needle-shaped crystals. The yield was 31%.

Anal. Calcd for Pt(phen)(CN)$_2$: C, 39.3; H, 1.9; N, 13.1. Found: C, 39.1; H, 1.9; N, 13.2. IR: ν(CN), 2120, 2105 cm^{-1}.

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Table I. Crystal Data and Refinement Parameters for Pt(bpy)(CN)$_2$ (**1**) and Pd(bpy)(CN)$_2$ (**2**)

	1	**2**
formula	$C_{12}H_8N_4Pt$	$C_{12}H_8N_4Pd$
fw	403.31	314.62
space group	$C2mm$ (No. 38)	
a, Å	9.357 (2)	9.387 (2)
b, Å	18.154 (5)	18.173 (3)
c, Å	3.3296 (4)	3.3541 (4)
V, Å^3	565.6 (2)	572.2 (1)
T, °C	20	20
Z	2	2
d_{measd}, g cm^{-3}	3.39	1.82
d_{calcd}, g cm^{-3}	3.368	1.826
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)	
abs coeff, cm^{-1}	125.13	15.80
transmission factors	0.047–0.103	0.570–0.660
$R(F_o)$	0.036	0.042
$R_w(F_o^2)$	0.037	0.051

Pd(bpy)(CN)$_2$. A mixture of Pd(CN)$_2$ (2 mmol) and 2,2'-bipyridine (14 mmol) in dimethylformamide (70 mL) was stirred and refluxed for 24 h. The reaction mixture was then cooled to room temperature and filtered to give white needle-shaped crystals, which were washed with dichloromethane to remove the unreacted free ligand. The yield was 80%.

Anal. Calcd for Pd(bpy)(CN)$_2$: C, 45.8; H, 2.5; N, 17.8. Found: C, 45.8; H, 2.5; N, 17.9. IR: ν(CN), 2135, 2130 cm^{-1}.

Pd(phen)(CN)$_2$. It is similarly prepared as its bpy analogue. The crude product could be recrystallized in hot dimethylformamide. The yield was 86%.

Anal. Calcd for Pd(phen)(CN)$_2$: C, 39.3; H, 1.87; N, 13.1. Found: C, 39.1; H, 1.86; N, 13.2. IR: ν(CN), 2140, 2130 cm^{-1}.

Crystallographic Study of Pt(bpy)(CN)$_2$ (1) and Pd(bpy)(CN)$_2$ (2). Data collection[7] and refinement parameters are summarized in Table I. Azimuthal scans of 18 selected strong reflections over a range of 2θ values were used to define a pseudoellipsoid for the application of absorption corrections.[8,9] The structure of **1** was solved by means of the heavy-atom method. The molecule occupies a site of $2mm$ symmetry: all atoms lie in the mirror plane z = 0, and the mirror plane y = 0 bisects the N(1)–Pt–N(1') and C(6)–Pt–C(6') bond angles and passes through the midpoint of the C(1)–C(1') bond. All non-hydrogen atoms in the asymmetric unit were subjected to anisotropic refinement. The aromatic H atoms were generated geometrically (C–H fixed at 0.96 Å), allowed to ride on their respective parent C atoms, and included in structure factor calculations with assigned isotropic thermal parameters (1.2 times the U_{eq} values of the corresponding C atoms). The structure of **2** was refined in the same manner.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL system.[10] Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed.[11]

The final atomic coordinates are listed in Table II. Selected bond distances and bond angles are given in Table III. Anisotropic thermal parameters, structure factors, and a packing diagram (Figure S1) are available as supplementary material.

Results and Discussion

Several synthetic methods for the bis(amine)dicyanoplatinum(II) complexes are known.[4b,6,12] In this work, we adopt the approach of Parkins and co-workers[6] and find that Pt(CN)$_2$·xH$_2$O reacts easily with substituted 2,2'-bipyridines or 1,10-phenanthrolines in refluxing dimethylformamide or pyridine to give cis-[Pt(diimine)(CN)$_2$]. The synthesis of Pd(diimine)(CN)$_2$ is similar, with Pd(CN)$_2$ used as the starting material.

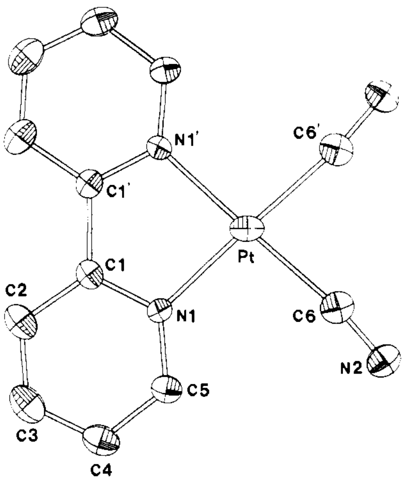

Figure 1. The Pt(bpy)(CN)$_2$ molecule (**1**) with atom numbering. The thermal ellipsoids are drawn at the 30% probability level.

The M(L-L)(CN)$_2$ (M = Pd, Pt; L-L = substituted 2,2'-bipyridines or 1,10-phenanthrolines) complexes are air-stable solids. Their solubilities in most organic solvents are low. However, the methyl groups in Pt(4,4'-Me$_2$Bpy)(CN)$_2$ render this solid more soluble in acetonitrile and methanol. The metal complexes adopt the cis configuration, as evidenced from their IR spectra, where two C≡N stretches are observed in each case.

X-ray Crystal Structures of Pt(bpy)(CN)$_2$ and Pd(bpy)(CN)$_2$. Figure 1 shows a thermal ellipsoid plot of the Pt(bpy)(CN)$_2$ molecule with atom numbering. The platinum coordination is essentially square planar: all atoms lie in the mirror plane z = 0, and the mirror plane y = 0 bisects the N(1)–Pt–N(1') and C(6)–Pt–C(6') angles and passes through the midpoint of the C(1)–C(1') bond. The Pt–N distance of 2.00 (1) Å is similar to those values found in Pt(bpy)Cl$_2$ [2.001 (6) Å][13] and Pt(bpy)$_2^{2+}$ [2.025 (4) and 2.028 (5) Å].[14] The measured Pt–C distance of 2.01 (2) Å is slightly longer than that in [Pt(phen)$_2$(CN)]$^+$ [1.931 (6) Å][15] but comparable to values of 1.99–2.008 (2) Å in K$_{1.75}$[Pt(CN)$_4$]·1.5H$_2$O.[16] As a result of the nonbonded repulsions between the CN groups themselves, a significantly nonlinear Pt—C≡N angle of 172.1 (18)° is found. The bond lengths and angles in the Pt-bpy unit are normal.

The crystal structure of Pt(bpy)(CN)$_2$ consists of a columnar stacking of superimposed planar monomeric units normal to the c axis. [Figure S1 (supplementary material) shows a stereodrawing of the crystal structure]. For this type of square-planar platinum(II) complex containing a continuous chain of metal atoms throughout the structure, the Pt···Pt distances[2,17] lie in the range of 3.09–3.50 Å [for example, 3.18 Å in Ca[Pt(ox)$_2$](H$_2$O)$_{3.5}$[18] and 3.45 Å in Pt(bpy)Cl$_2$[13]]. Thus, Pt(bpy)(CN)$_2$ with a Pt···Pt distance of c = 3.3296 Å may be thought of as an intermediate case.

The structure of Pd(bpy)(CN)$_2$ is isomorphous to its platinum analogue. A comparison between the Pt and Pd structures reveals some interesting features. The respective Pd–C(CN) and Pd–Pd distances of 2.12 (1) and 3.3541 (4) Å are longer than the corresponding values in Pt(bpy)(CN)$_2$ despite the larger atomic radius of Pt over Pd, whereas the C≡N distance of 1.10 (2) Å in the Pd complex is about 0.01 Å shorter than that in the Pt case, 1.20 (3) Å. This finding may suggest that metal (d$_\pi$(M)) to ligand

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Table II. Fractional x and y Atomic Coordinates ($\times 10^4$) and Thermal Parameters[a] ($Å^2 \times 10^4$ for M; $Å^2 \times 10^3$ for Other Atoms) of M(bpy)$(CN)_2$ (**1**, M = Pt; **2**, M = Pd)

	1			**2**		
atom	x	y	U_{eq} or U	x	y	U_{eq} or U
M	0	0	432 (1)*	0	0	419 (2)*
N(1)	1585 (13)	740 (8)	38 (1)*	1531 (10)	716 (9)	35 (2)*
C(1)	2861 (10)	412 (5)	42 (1)*	2812 (7)	411 (4)	42 (2)*
C(2)	4108 (3)	841 (8)	54 (2)*	4076 (10)	839 (6)	61 (3)*
C(3)	3995 (15)	1587 (9)	67 (2)*	3933 (13)	1591 (7)	78 (4)*
C(4)	2664 (15)	1916 (7)	64 (2)*	2598 (12)	1913 (5)	67 (3)*
C(5)	1468 (12)	1459 (5)	48 (2)*	1464 (9)	1471 (4)	49 (2)*
C(6)	−1640 (22)	719 (14)	48 (2)*	−1725 (13)	750 (11)	49 (3)*
N(2)	−2490 (13)	1211 (6)	59 (2)*	−2528 (9)	1192 (4)	59 (2)*
H(2)	5031	610	65	4995	607	72
H(3)	4841	1886	79	4768	1896	93
H(4)	2566	2443	73	2492	2438	80
H(5)	533	1677	58	538	1695	59

[a] Asterisk indicates equivalent isotropic tempreature factor U_{eq} defined as one-third of the trace of the orthogonalized U matrix. The exponent of the isotropic temperature factor takes the form $-8\pi^2 U(\sin^2\theta)/\lambda^2$.

Table III. Bond Lengths (Å) and Bond Angles (deg)[a] in M(bpy)$(CN)_2$ (**1**, M = Pt; **2**, M = Pd)

	1	**2**		**1**	**2**
M–N(1)	2.00 (1)	1.94 (1)	M–C(6)	2.01 (2)	2.12 (1)
N(1)–C(1)	1.33 (2)	1.32 (1)	C(1)–C(1′)	1.50 (2)	1.50 (1)
C(1)–C(2)	1.40 (2)	1.42 (1)	C(2)–C(3)	1.36 (2)	1.37 (2)
C(3)–C(4)	1.38 (2)	1.38 (2)	C(4)–C(5)	1.39 (2)	1.33 (1)
C(5)–N(1)	1.31 (2)	1.37 (2)	C(6)–N(2)	1.20 (3)	1.10 (2)
N(1)–M–C(6)	97.4 (8)	97.8 (6)	N(1)–M–N(1′)	84.3 (8)	84.3 (8)
C(6)–M–C(6′)	80.8 (13)	80.1 (9)	M–N(1)–C(1)	111.3 (9)	113.1 (10)
M–N(1)–C(5)	127.4 (9)	129.6 (8)	C(1)–N(1)–C(5)	121.3 (11)	117.3 (10)
N(1)–C(1)–C(2)	119.8 (11)	122.1 (9)	N(1)–C(1)–C(1′)	116.5 (7)	114.7 (7)
C(2)–C(1)–C(1′)	123.7 (7)	123.2 (5)	C(1)–C(2)–C(3)	119.2 (11)	117.6 (9)
C(2)–C(3)–C(4)	120.1 (13)	120.6 (11)	C(3)–C(4)–C(5)	117.8 (12)	118.0 (9)
N(1)–(5)–C(4)	121.8 (11)	124.4 (8)	M–C(6)–N(2)	172.1 (18)	173.2 (13)

[a] The primed atoms are related to the unprimed atoms by the mirror plane at $y = 0$.

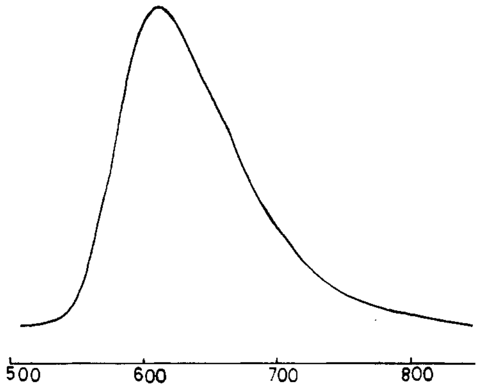

Figure 2. Room-temperature solid-state emission spectrum of Pt(bpy)$(CN)_2$ (red). The excitation is at 350 nm.

(π^*(CN)) π-back-bonding, which strengthens the M–C bond but weakens the C≡N bond, is less important in the Pd(II) system. Alternatively, the differences in bond lengths are probably due to relativistic effects acting principally on the 6s σ component of the metal–ligand bond for platinum.[19] The 6s σ component for Pt–Pt interaction in the solid is also probably responsible for the shorter M–M distance.

Solid-State Spectroscopic Properties. The Pt(L-L)$(CN)_2$ solids are intensely colored [L-L = 4,4′-Me_2bpy, yellow; L-L = bpy, orange red; L-L = phen, violet] despite the fact that these species exhibit weak absorptions at wavelengths longer than 350 nm in solution. [The UV-vis spectrum of Pt(phen)$(CN)_2$ in dimethylformamide is shown in Figure S2 (supplementary material).] We attribute the color of the Pt(II) solids to the low-energy transition arising as a consequence of metal–metal interaction in the solid state.[20] The change in color from Pt(4,4′-Me_2bpy)$(CN)_2$ (yellow) to Pt(phen)$(CN)_2$ (violet) is likely due to the different intermolecular Pt–Pt distances and the fact that the repulsive steric effect of the methyl groups in the 4,4′-Me_2bpy system would hinder the approach of the Pt atoms.

The Pt(II) solids are strongly emissive. The solid-state emission spectrum of Pt(bpy)$(CN)_2$ is shown in Figure 2. The violet Pt(phen)$(CN)_2$ and orange-red Pt(bpy)$(CN)_2$ solids show emissions at λ_{max} of 610 and 670 nm, respectively, which are not observed in solutions of these Pt(II) complexes. The measured lifetime for the 610-nm emission of Pt(bpy)$(CN)_2$ is 0.24 μs at room temperature. The emission of the Pt(4,4′-Me_2bpy)-$(CN)_2 \cdot 2H_2O$ solid depends on its crystalline form. It is usually yellow (sometimes orange), and in this case, emission at 570 nm ($\tau_0 \sim$ 0.5–0.6 μs at room temperature) is found. However, a pale yellow form is sometimes obtained during recrystallization in acetonitrile. This pale yellow solid shows a vibronic emission at λ_{max} ~500 nm (Figure S3, supplementary material), which is likely derived from the internal ligand $\pi\pi^*$ triplet.[21]

The Pd(L-L)$(CN)_2$ solids, on the other hand, are virtually colorless. They are not emitting solids when compared to their platinum analogues.

Acknowledgment. Financial support from the University of Hong Kong and the Croucher Foundation (C.-M.C., L.-Y.H., and C.-K.P.) is gratefully acknowledged.

Supplementary Material Available: Tables IV and V, listing additional crystal data and anisotropic thermal parameters for **1** and **2**, and Figures S1–S3, showing a unit cell stereodrawing, UV-vis spectrum, and emission spectrum for **1** (5 pages); listings of structure factors for **1** and **2** (9 pages). Ordering information is given on any current masthead page.

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(21) Upon excitation of the Pd(bpy)$(CN)_2$ solid at 300–350 nm, some very weak and broad emissions at 600–650 nm are found, the nature of which is uncertain.