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Tetracyanometalates of Ni, Pd, and Pt with Cyclic Diquaternary Cations of 2,2′-Bipyridine and 1,10-Phenanthroline. A Vibrational, Crystallographic, and Theoretical Study of Intermolecular Weak Interactions

Pablo Vitoria,[‡] Javier I. Beitia,[*,†] Juan M. Gutiérrez-Zorrilla,[*,‡] Emilio R. Sáiz,[†] Antonio Luque,[‡] Maite Insausti,[‡] and José J. Blanco[‡]

Departamento de Química Inorgánica, Facultad de Farmacia, Universidad del País Vasco, Apartado 450, 01080 Vitoria, Spain, and Departamento de Química Inorgánica, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

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The compounds (bpy-dq)[Ni(CN)$_4$]·2H$_2$O (**1**), (bpy-dq)[Pd(CN)$_4$]·2H$_2$O (**2**), and ((bpy-dq)[Pt(CN)$_4$]·2H$_2$O (**3**) (bpy-dq = $(C_{12}H_{12}N_2)^{2+}$, 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium) and (phen-dq)[Ni(CN)$_4$] (**4**), (phen-dq)[Pd(CN)$_4$]·H$_2$O (**5**), and (phen-dq)[Pt(CN)$_4$]·H$_2$O (**6**) (phen-dq = $(C_{14}H_{12}N_2)^{2+}$, 5,6-dihydropyrazino[1,2,3,4-*lmn*]-1,10-phenanthrolinediium) have been synthesized and characterized by X-ray diffraction. The three bipyridinium diquaternary salt derivatives are isostructural. The crystal structures of these dihydrated compounds consist of columns formed by alternating anion complexes and diquaternary cations, π–π interacting through cyanide ligands and the aromatic rings, and stabilized by an extended hydrogen-bond network. On the other hand, the packing in the phenanthrolinium diquaternary salt derivatives is strongly dependent on the hydration degree. Thus, the anhydrous $[Ni(CN)_4]^{2-}$ compound presents a laminar arrangement and the hydrated salts show a columnar packing, similar but not the same as compounds **1**–**3**. The anhydrous form of compound **5** is isostructural with compound **4**. Vibrational (IR, Raman) and thermogravimetric studies of these compounds have been carried out. Finally, DFT calculations have been performed on the isolated tetracyanometalate anions and diquaternary cations to assign the fundamental modes in the vibrational spectra. The intermolecular weak interactions were studied through the analysis of the charge density by using the theory of atoms in molecules (AIM).

Introduction

Ion pair charge transfer (IPCT) complexes of the type $\{A^{2+}[ML_2]^{2-}\}$, wherein the acceptor A^{2+} is a dicationic bipyridinium or phenanthrolinium derivative and $[ML_2]^{2-}$ is a planar metal dithiolene, form an interesting subclass of donor−acceptor systems which have been reported by Kisch et al.[1] The redox properties of these compounds can be tuned depending on the metal M, the ligand L, and the nature of the acceptor cation.

In the course of our study on charge-transfer ion pairs we have investigated systems derived of *o*-phenylenebis(oxamato)cuprate(II), $[Cu(opba)]^{2-}$, and various cyclic diquaternary cation salts of the formula (phen-dq)[Cu(opba)]·3H$_2$O and Na$_2$(bpy-dq)[Cu(opba)]$_2$·4H$_2$O. These compounds exhibit ion-pair charge-transfer (IPCT) bands in the region 400−600 nm both in the solid state and in aqueous solution.[2] Recently we have extended our study to tetracyanometalates of diquaternary cations.

The structural data available for the 4,4′-bipyridinium and phenanthrolinium salts show that there are several possibilities of charge dissipation through different types of hydrogen

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* Author to whom correspondence should be addressed. E-mail: qipguloj@lg.ehu.es.

[‡] Facultad de Ciencias.

[†] Facultad de Farmacia.

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10.1021/ic0200287 CCC: $22.00

Table 1. Selected Experimental and Theoretical IR and Raman Bands (cm^{-1}) for Compounds **1**−**6**

$M(CN)_4^{2-}$ Anions

$Ni(CN)_4^{2-}$			$Pd(CN)_4^{2-}$			$Pt(CN)_4^{2-}$			symmetry and assignment	
1	**4**	DFT	**2**	**5**	DFT	**3**	**6**	DFT		
2142	2133	*2139*	2157	2148	*2152*	2156	2155	*2162*	A_{1g}(R)	$\nu_s(C\equiv N)$
2132	2123	*2129*	2149	2137	*2135*	2140	2137	*2138*	B_{1g}(R)	$\nu_{as}(C\equiv N)$
2127	2113	*2124*	2139	2127	*2129*	2136	2123	*2128*	E_u(IR)	$\nu_{as}(C\equiv N)$
2116			2129			2127				
		403			*473*	495	495	*497*	E_u(IR)	$\nu_{as}(M-C)$
398	396	*374*	417	417	*392*	461	456	*442*	A_{1g}(R)	$\nu_s(M-C)$
303	313	*298*	294	291	*294*	317	317	*326*	E_g(R)	$\delta_{oop}(M-CN)$
296	295		286							
		109			*101*			*109*	B_{2g}(R)	$\delta(C-M-C)$

Diquaternary Cations (Raman Spectra)

bpy-dq					phen-dq				
1	**2**	**3**	DFT	symmetry	**4**	**5**	**6**	DFT	symmetry
743	743	740	*756*	A	608		617	*618*	A
733	733	738	*741*	A	590	592	592	*594*	A
645	645	645	*657*	B	546			*551*	A
608	608	606	*610*	B	539	538	539	*546*	A
550	550	550	*557*	A	516		517	*511*	B
537	537	536	*543*	A	505	502	503	*500*	B
498	498	498	*503*	B	464		456	*463*	B
398	397	396	*398*	A	431	434	433	*438*	A
389	389	389	*397*	B	393	394	394	*397*	A
316	314	317	*315*	A	217	223	221	*217*	A
278	277	277	*276*	A				*200*	B
217	219	216	*199*	B					
196	200	192	*181*	A					

bonds in which the nitrogen end of cyano ligands, water molecules, and the nitrogen atoms of pyridine rings participate.[3] It was also found that electronic charge can be transferred through the π stack systems of the aromatic rings.

In the present paper we describe the synthesis and crystal structure of tetracyanometalates(II) (M = Ni, Pd, and Pt) with the *N*,*N*′-alkylated derivatives of 2,2′-bipyridine, bpy-dq (bpy-dq = 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinium) and 1,10-phenanthroline, phen-dq (phen-dq = 5,6-dihydropyrazino[1,2,3,4-*lmn*]- 1,10-phenanthrolinium). The X-ray crystal structures, thermal behavior, and vibrational study, including a theoretical analysis with density functional theory, are presented.

These compounds may be used as precursors in the synthesis of radical−cation salts which could contain stacks of partially oxidized $[M(CN)_4]^{x-}$ ions with strong overlap between the metal atoms.[4]

Results and Discussion

Vibrational Spectra. The IR spectra are dominated by the bands of cation which change their position and intensity in comparison to the cation bromide. This can be explained by hydrogen bonding to anion. The hydrated compounds show a strong absorption in the range 3600−3100 cm^{-1} that certifies the existence of the O−H bonds from the water molecules.

The $[M(CN)_4]^{2-}$ anion possesses ideally D_{4h} symmetry and, thus, will have 16 fundamental vibrations (2 A_{1g}, 1 A_{2g}, 2 B_{1g}, 2 B_{2g}, 1 E_g, 2 A_{2u}, 2 B_{2u}, and 4 E_u).[5] Of these, A_{2u} and E_u are infrared active, while A_{1g}, B_{1g}, B_{2g}, and E_g are Raman active. The A_{2g} and B_{2u} vibrations are inactive. No B_{2g} modes were observed. To be able to assign all the bands of the tetracyanometalate anions, density functional calculations (DFT) have been carried out for all of them assuming ideal D_{4h} symmetry. In Table 1 are listed the experimental and theoretical (DFT calculations) IR and Raman bands for the anion complexes and the most intense low-frequency region Raman bands for the diquaternary cations. The corresponding Raman spectra are shown in Figure 1. As can be seen in Table 1 the agreement for the diquaternary cations is remarkable. This fact strongly indicates that the method chosen for the calculations is good and has allowed us a better assignment of the bands corresponding to the anion complexes and to see the variation of the bands upon changing the central metallic atom.

The strong absorption in IR, near 2125 cm^{-1}, is associated with C≡N stretching vibrations. The A_{1g} and B_{1g} C≡N stretching modes are observed in the Raman spectrum between 2160 and 2120 cm^{-1}.

In the low-frequency region of the IR spectra the only observed band corresponds to $\nu_{as}(Pt-C)$, since for Ni and Pd the theoretical calculations indicate that the band is either located below 400 cm^{-1} (Ni) or it is very weak (Pd), making it very hard to observe. In the Raman spectra below 500

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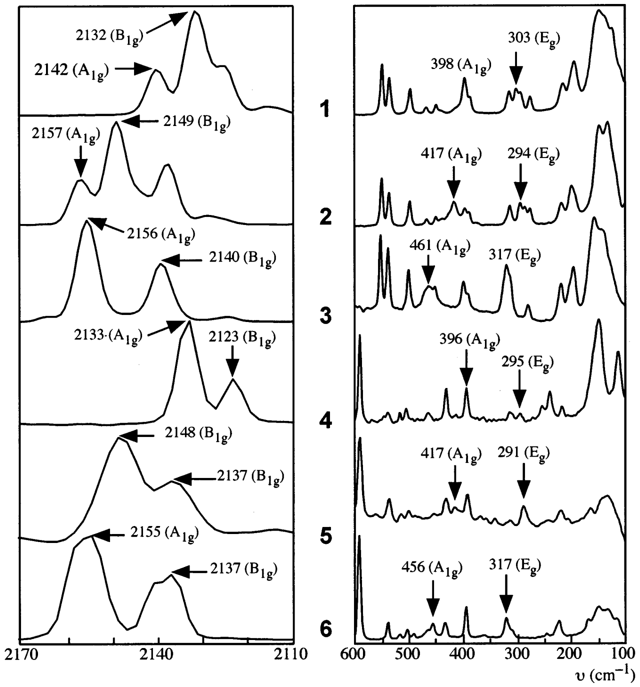

Figure 1. Raman spectra of the compounds with tetracyanometalate asignations.

cm^{-1} the A_{1g} and E_g M−CN group associated vibrations are observed. The most remarkable fact is the strong blue-shift of these vibrations for the Pt compound, specially the A_{1g} one, as corroborated by the calculations (see Table 1) and in good agreement with the results for potassium salts.[5] As the A_{1g} vibration is a metal−carbon stretching one, its frequency should correlate with the strength of this bond. AIM calculations over $[M(CN)_4]^{2-}$ anions confirm this fact and show a nice correlation between the A_{1g} mode frequency and the value of the electron density at the M−C bond critical point, which is 0.1116, 0.1133, and 0.1270 au for M = Ni, Pd, and Pt, respectively.

Crystal Structures of Bipyridinium Derivatives: (bpy-dq)$[M(CN)_4]\cdot 2H_2O$ (1−3). The single-crystal structure determinations of bipyridinium derivative salts, $(C_{12}H_{12}N_2)[M(CN)_4]\cdot 2H_2O$ (**1** and **3**), show that both salts are isostructural. The asymmetric unit consists of one $(C_{12}H_{12}N_2)^{2+}$ bipyridinium diquaternary cation, one $[M(CN)_4]^{2-}$ complex anion, and two water molecules.

The structures of the complex dianion and the cation with the atomic numbering scheme are shown in Figure 2a. Selected bond lengths and angles are listed in Table 2.

In the $[M(CN)_4]^{2-}$ anion the metal atom is bonded to four CN^- ligands with a coordination approximately square planar. The M−C bond distances and C−M−C and M−C−N bond angles agree well with previously reported values for other Ni(II) and Pt(II) tetracyanometalates.[6]

The $(C_{12}H_{12}N_2)^{2+}$ bipyridinium diquaternary cation is not strictly planar. The two pyridinium rings are each very nearly planar, but the dihedral angle between the two aromatic rings is 19.5° and 19.2° for **1** and **3**, respectively, due to the ethylene bridge between the nitrogen atoms. Bond distances and angles within the organic cation are comparable with those reported in the literature.[7]

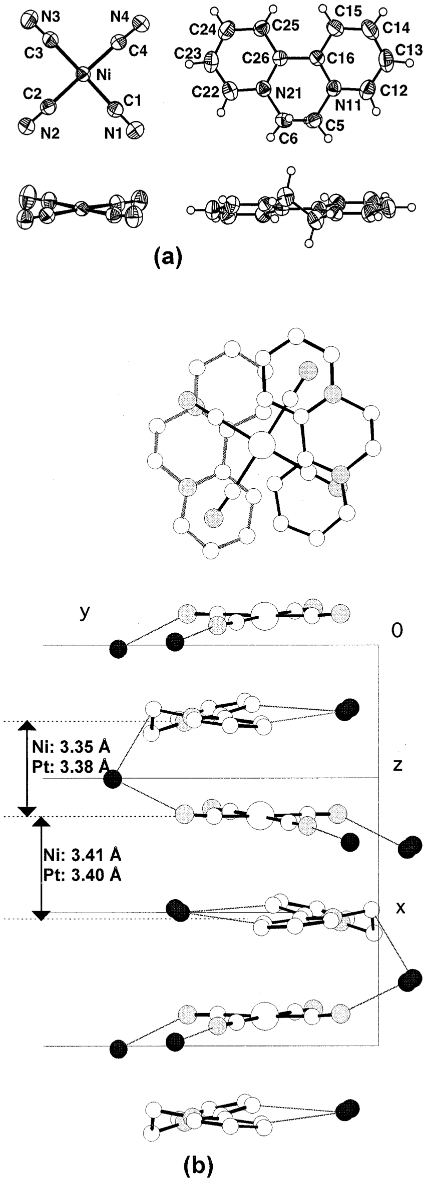

Figure 2. (a) ORTEP view with atom labeling for compounds **1** (Ni) and **3** (Pt). (b) Top and side view of a column with the interplanar distances.

The crystal structure of these compounds consists of columns of alternating cations and anions along the [101] direction (Figure 2b). An interesting structural feature is the stacking distance among anions and cations. Each anion is placed between two cations with the cyanide ligands sandwiched between the aromatic rings of two contiguous cations, probably due to $\pi-\pi$ interactions (Figure 2c).

The structure is stabilized by an extended hydrogen bond network of the type C−H···N, C−H···O, O−H···N, and O−H···O, involving the carbon of cations, nitrogens of cyanide anions, and water molecules. Anions and cations packed in the same column are linked via a water molecule

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Table 2. Experimental and Theoretical Bond Lengths (Å) and Angles (deg) and Hydrogen Contacts for Bpy-dq Compounds **1**−**3**

	$Ni(CN)_4^{2-}$		$Pd(CN)_4^{2-}$	$Pt(CN)_4^{2-}$	
	1	DFT	DFT	**3**	DFT
M−C1	1.864(3)	*1.886*	2.019	1.99(2)	*2.007*
M−C2	1.868(3)			1.97(3)	
M−C3	1.861(3)			1.97(2)	
M−C4	1.878(3)			2.00(3)	
C1−N1	1.140(4)	*1.194*	1.193	1.13(3)	*1.193*
C2−N2	1.144(5)			1.17(4)	
C3−N3	1.150(5)			1.16(3)	
C4−N4	1.138(5)			1.13(4)	
C1−M−C2	90.4(1)	*90*	90	90.5(1)	*90*
C2−M−C3	88.6(1)			88.1(9)	
C3−M−C4	92.4(1)			93.1(1)	
C1−M−C4	88.7(1)			88.3(9)	
C1−M−C3	177.9(2)			178(1)	
C2−M−C4	178.2(1)			178(1)	
M−C1−N1	176.1(3)	*180*	180	177(2)	*180*
M−C2−N2	178.7(3)			179(3)	
M−C3−N3	177.0(3)			177(2)	
M−C4−N4	178.0(3)			179(2)	

Hydrogen Contacts

	D···A/Å	
donor−H···acceptor	**1**	**3**
C12−H12···N4[a]	3.446(5)	3.43(3)
C13−H13···N1[b]	3.328(6)	3.39(4)
C14−H14···N2[b]	3.387(5)	3.36(4)
C24−H24···N4[c]	3.315(5)	3.39(3)
C25−H25···O1[d]	3.241(4)	3.25(3)
C15−H15···O1[d]	3.404(4)	3.41(3)
C6−H61···O1[e]	3.274(5)	3.21(3)
O1−H111···N1[e]	2.946(4)	2.93(3)
O2−H211···N3[f]	2.834(5)	2.80(3)
O2−H212···N2[g]	2.930(5)	2.92(3)
O1−H112···O2[b]	2.809(6)	2.83(4)

[a] $1 - x, -y, -z$. [b] $1 + x, y, z$. [c] $-^1/_2 + x, ^1/_2 - y, ^1/_2 + z$. [d] $-^1/_2 + x, ^1/_2 - y, -^1/_2 + z$. [e] $1 - x, -y, 1 - z$. [f] $^1/_2 - x, -^1/_2 + y, ^1/_2 - z$. [g] $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$.

with hydrogen contacts of the type C6−H61···O1 and O1−H111···N1. Ions belonging to different columns are linked by hydrogen contacts of the type C−H···N and hydrogen bonds involving the water molecules. Details of the H-bonding network are listed in Table 2.

In the case of compound **2**, high-quality crystals were not obtained. The X-ray diffraction pattern of the microcrystalline product was performed in the 2θ range between 5° and 70°. Indexation of the diffraction profile and refinement of the cell parameters and the atomic coordinate of palladium were made by FULLPROF,[8] on the basis of the space group $P2_1/n$ and the structural model found for compound **3**. The obtained parameters are described in Table 5. From these data, we can consider the three phases to be isostructural.

Crystal Structures of Phenanthrolinium Derivatives: (phen-dq)[Ni(CN)$_4$] (4). The asymmetric unit of phenanthrolinium derivative anhydrous salt $(C_{14}H_{12}N_2)[Ni(CN)_4]$, **4**, consists of one phenanthrolinium diquaternary cation, $(C_{14}H_{12}N_2)^{2+}$, and one $[Ni(CN)_4]^{2-}$ complex anion.

Table 3. Selected Bond Lengths (Å) and Angles (deg) and Hydrogen Bonds for Compounds **4** and **6**

4		**6**	
Ni−C1	1.879 (4)	Pt1−C1	1.992 (4)
Ni −C2	1.854 (7)	Pt1−C2	1.996 (4)
Ni −C3	1.859 (6)	Pt2−C3	1.992 (4)
		Pt2−C4	1.989 (4)
C1−N1	1.133 (6)	C1−N1	1.127 (4)
C2−N2	1.142 (8)	C2−N2	1.135 (5)
C3−N3	1.140 (9)	C3−N3	1.135 (4)
		C4−N4	1.149 (5)
C1−Ni −C2	88.4 (1)	C1−Pt1−C2	90.07 (2)
C2−Ni−C3	180.0 (1)	C3−Pt2−C4	89.7 (1)
C1−Ni−C3	91.6 (1)	C3′−Pt2−C4	90.3 (1)
		Pt1−C1−N1	178.2 (3)
Ni−C1−N1	177.7 (4)	Pt1−C2−N2	177.9 (4)
Ni−C2−N2	180.0 (1)	Pt2−C3−N3	177.7 (3)
Ni−C3−N3	180.0 (1)	Pt2−C4−N4	178.6 (3)

Hydrogen Contacts

4		**6**	
donor−H···acceptor	D···A/Å	donor−H···acceptor	D···A/Å
C12−H12···N1[a,b]	3.428 (6)	C22−H22···O1	3.183 (6)
C13−H13···N2[a−d]	3.247 (5)	C23−H23···N2	3.274 (7)
C18−H181···N1[a,b]	3.378 (6)	C28−H281···O1	3.433 (5)
C13−H13···N3[e−h]	3.250 (5)	O1−H1···N3	3.048 (5)
C17−H17···N1[e,f]	3.477 (6)	O1−H2···N1	3.064 (4)
C18−H182···N3[i−l]	3.369 (7)	C24−H24···N3[m]	3.499 (6)
C18−H182···N2	3.471 (7)	C27−H27···N1[n]	3.363 (5)
		C13−H13···N3[o]	3.318 (5)
		C18−H181···N2[p]	3.348 (5)

[a] $1 - x, 1 - y, -z$. [b] $^1/_2 + x, 1 - y, -z$. [c] $^1/_2 + x, 1 - y, -^1/_2 + z$. [d] $1 - x, 1 - y, -^1/_2 + z$. [e] $1 - x, -y, -z$. [f] $^1/_2 + x, -y, -z$. [g] $^1/_2 + x, -y, -^1/_2 + z$. [h] $1 - x, -y, -^1/_2 + z$. [i] $x, 1 + y, z$. [j] $^1/_2 - x, 1 + y, z$. [k] $^1/_2 - x, 1 + y, ^1/_2 - z$. [l] $x, 1 + y, ^1/_2 - z$. [m] $1 - x, 1 - y, 1 - z$. [n] $1 - x, ^1/_2 + y, ^1/_2 - z$. [o] $1 + x, ^1/_2 - y, -^1/_2 + z$. [p] $1 - x, -^1/_2 + y, ^1/_2 - z$.

Table 4. Properties of the Critical Points in the Electron Density for Compounds **1** and **4**

(bpy-dq)[Ni(CN)$_4$]·2H$_2$O (**1**)

critical point[a]	from → to[b]	ρ[c]	$\nabla^2\rho$[d]	ϵ[e]	type
1	C4 to C15−H15 bcp	0.00501	0.01624	4.070	$\pi-\pi$
2	C3 to C15	0.00660	0.01864	0.558	$\pi-\pi$
3	N2 to N21	0.00588	0.01828	6.530	$\pi-\pi$
4	C2 to C26	0.00553	0.01624	0.924	$\pi-\pi$
5	N3 to H62	0.00199	0.00756	0.196	HB (vw)

(phen-dq)[Ni(CN)$_4$] (**4**)

critical point	from → to	ρ	L	ϵ	type
1	Ni to C17−C17 bcp	0.00625	0.02280	1.467	$\pi-\pi$
2	N1 to C14	0.00469	0.01360	2.622	$\pi-\pi$
3	N2 to C16−C16 bcp	0.00678	0.01912	1.680	$\pi-\pi$
4	N1 to C14	0.00468	0.01360	2.294	$\pi-\pi$
5	N2 to H182	0.00856	0.02736	0.068	HB (vw)

[a] Labels of critical points as in Figure 5. [b] Bond path. [c] Electronic density (au). [d] Laplacian. [e] Ellipticity.

Figure 3a shows the structures of the complex dianion and the cation with the atomic labeling scheme. Selected bond lengths and angles are listed in Table 3. The Ni−C bond distances and C−Ni−C and Ni−C−N bond angles agree well with values previously reported for other tetracyanonickelates.[6]

In the $(C_{14}H_{12}N_2)^{2+}$ phenanthroline diquaternary cation the aromatic rings are coplanar and lie on a crystallographic mirror plane. There is another crystallographic mirror perpendicular to the molecule. The C18 atom, which is placed 0.393 Å out of the molecular mean plane, is

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Table 5. Crystal Data and Details of the Structure Determination of Compounds

(bpy-dq)[M(CN)$_4$]·2H$_2$O

	1[a]	**2**[b]	**3**[a]
formula	$C_{16}H_{12}N_6Ni\cdot 2H_2O$	$C_{16}H_{12}N_6Pd\cdot 2H_2O$	$C_{16}H_{12}N_6Pt\cdot 2H_2O$
fw	383.04	430.76	519.431
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	9.223(1)	9.183(1)	9.147(1)
b/Å	15.689(2)	15.860(1)	15.847(6)
c/Å	12.161(4)	12.403(1)	12.511(2)
β/deg	102.39(2)	103.54(5)	104.04(2)
V/Å^3	1718.7(6)	1755.9(3)	1759.3(8)
Z	4	4	4
$D_x/g\cdot cm^{-3}$	1.480		1.961
μ(Mo Kα)/cm^{-1}	11.534		79.98
reflns collected	5009		5092
obsd reflns	3143	303	2069
R	0.043		0.058
wR(F)	0.052		0.062
R_B		7.79	
R_{WP}		12.0	

(phen-dq)[M(CN)$_4$]·nH$_2$O, ($n = 0, 1$)

	4[a]	**5b**[b]	**5**[b]	**6**[a]
formula	$C_{18}H_{12}N_6Ni$	$C_{18}H_{12}N_6Pd$	$C_{18}H_{12}N_6Pd\cdot H_2O$	$C_{18}H_{12}N_6Pt\cdot H_2O$
fw	371.05	418.75	436.76	525.438
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$Pmnm$ (no. 59)	$Pmnm$ (no. 59)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	6.555(2)	6.669(2)	8.603(2)	9.928(2)
b/Å	9.426(2)	9.586(2)	14.717(3)	14.754(2)
c/Å	12.436(2)	12.495(2)	14.959(3)	12.046(4)
β/deg			108.88(1)	100.98(1)
V/Å^3	768.4(3)	798.8(3)	1786.0(6)	1732.2(7)
Z	2	2	4	4
$D_x/g\cdot cm^{-3}$	1.604			2.015
μ(Mo Kα)/cm^{-1}	1.276			8.121
reflns collected	1259			5029
obsd reflns	830	144	161	2441
R	0.0460			0.0336
wR(F^2)	0.1354			0.0968
R_B		3.57	2.07	
R_{WP}		14.4	16.1	

[a] Single-crystal X-ray diffraction analysis. [b] Powder X-ray diffraction data.

disordered over four positions due to the above-mentioned crystallographic symmetry. Bond distances and angles within the diquaternary cation are comparable with those reported in the literature.[9]

The crystal structure is a bidimensional framework constructed from parallel layers located at two different x levels, $x = 0.25$ and 0.75. Each anion is surrounded by four cations and connected by eight C−H···N hydrogen bonds (Figure 3b). As can see in Figure 3c, the tetracyanonickelate complexes are sandwiched by two diquaternary cations at a distance of 3.227 Å, denoting a kind of $\pi-\pi$ interaction.

Anhydrous compounds **5b** and **6b** were thought to be isostructural to the previously described compound. X-ray powder diffraction patterns were taken for both as high-quality crystals were not obtained. Rietveld profile refinement was performed for **5b** with the FULLPROF[8] program (pattern matching analysis), on the basis of the orthorhombic cell, space group *Pmnm*, and the cell parameters found for compound **4**. Taking into account the obtained values, which are given in Table 5, it can be deduced that it is in fact isostructural. On the other hand, the profile refinement of the diffraction pattern for compound ($C_{14}H_{12}N_2$)[Pt(CN)$_4$], **6b**, has not yielded good results. It seems that the compound presents a great tendency to hydration and that some of the diffraction peaks correspond to the hydrated phase. Further treatments with high-temperature diffraction have not yielded a unique nonhydrated phase.

(phen-dq)[M(CN)$_4$]·H$_2$O [M = Pd, Pt] (5, 6). The single-crystal structure determination of 5,6-dihydropyrazino[1,2,3,4-*lmn*]-1,10-phenanthrolinium tetracyanoplatinate, ($C_{14}H_{12}N_2$)-[Pt(CN)$_4$]·H$_2$O, **6**, shows that the asymmetric unit consists of two centrosymmetric [Pt(CN)$_4$]$^{2-}$ complex anions: one diquaternary phenanthrolinium dication and one water molecule. For the palladium compound **5**, as high quality crystals were not obtained, X-ray powder diffraction data were used to obtain structural information. The space group found for compound **6** and unit cell parameters obtained by DICVOL91[10] have been used to perform the pattern matching analysis. The calculated values are present in Table 5.

Figure 4a shows the structures of the complex dianion and the cation with the atomic numbering scheme. Selected bond

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(9) Summers, L. A. *Tetrahedron* **1968**, *24*, 5433.

(10) Boultiff, A.; Louer, D. *J. Appl. Crystallogr.* **1991**, *24*, 987.

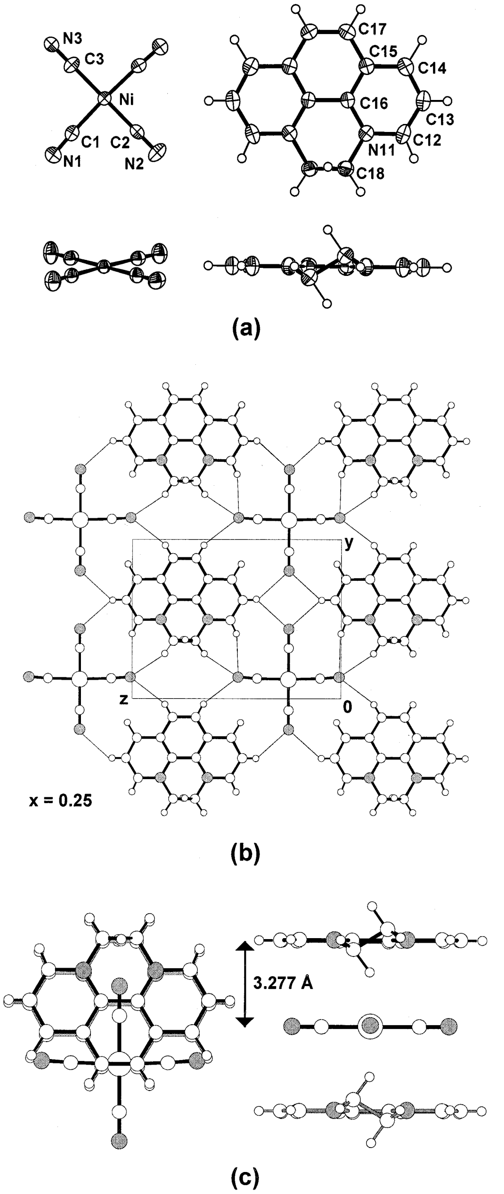

Figure 3. Compound **4**: (a) ORTEP view with atom labeling, (b) Arrangement in a shell ($x = 0.25$) showing the hydrogen bonding network. (c) Top and side view of the $\pi-\pi$ interactions.

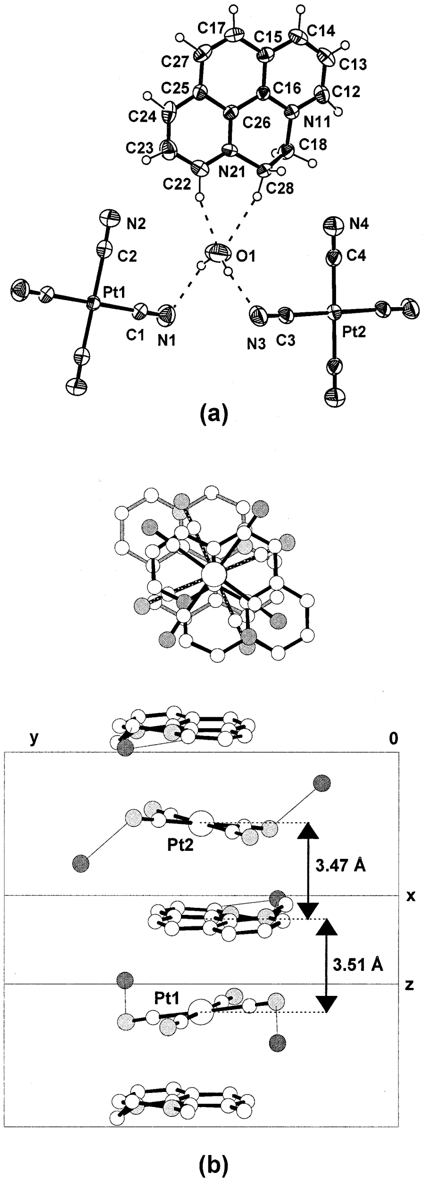

Figure 4. Compound **6**: (a) ORTEP view of an asymmetrical unit together with atom labeling showing the water molecule environment. (b) Top and side view of a column with the interplanar distances.

lengths and bond angles are listed in Table 3. The Pt−C bond distances and C−Pt−C and Pt−C−N bond angles agree well with values previously reported for other tetracyanoplatinates.[6]

The $(C_{14}H_{12}N_2)^{2+}$ phenanthroline diquaternary cations are not planar and the dihedral angles between the aromatic rings range from 3.30° to 9.87°. Bond distances and angles within the organic cation are comparable with those reported in the literature.[9]

The crystal structure consists of columns of alternating cations and anions along the [101] direction (Figure 4b). Each anion is placed between two cations at 3.47 and 3.51 Å, with the cyanide ligands sandwiched between the aromatic rings of two contiguous cations. In this case cation and anions are not as parallel as in the previous compounds, the angle between the mean planes of the anion and the cation being 7.55° for Pt1 and 11.10° for Pt2.

Intermolecular Weak Interactions. The possible presence of intermolecular weak interactions was studied through the analysis of the charge density by using the theory of atoms in molecules (AIM),[11] which has been shown, both in experimental and theoretical studies, to be able to highlight the dominant interactions which contribute to weak binding forces.[12]

Calculations have been performed on the nickel compounds **1** and **4**, using the crystallographically determined geometries. The system studied in compound **1** includes a tetracyanonickelate anion sandwiched between two bipyridine diquaternary cations and seven water molecules, whereas for the centrosymmetric compound **4** just the tetracyano-

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(11) Bader, R. F. W. *Atoms in molecules−A quantum theory*; International Series of Monographs on Chemistry, No. 22; Oxford University Press: Oxford, UK, 1990.

(12) Bone, R. G. A.; Bader, R. F. W. *J. Phys. Chem.* **1996**, *10*, 10892.

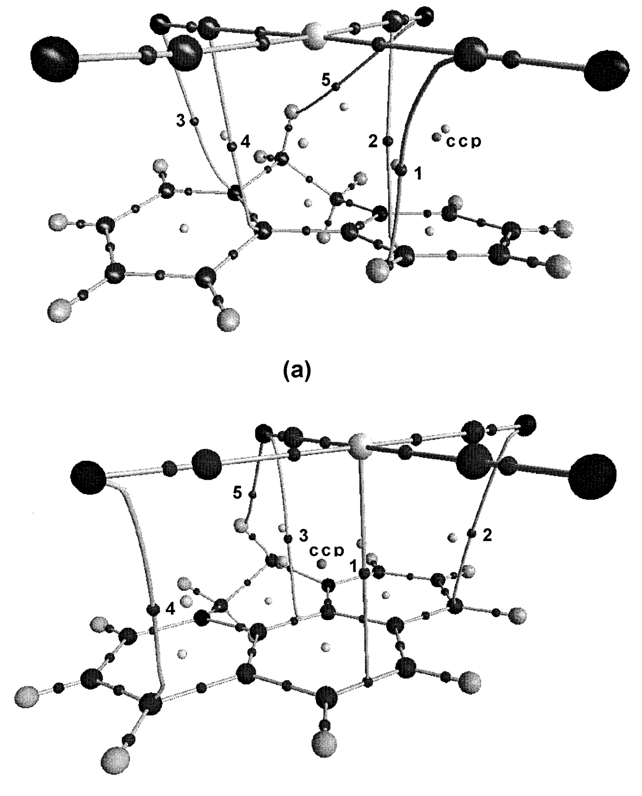

Figure 5. Molecular graphs determined by the topology of the electron density for (a) compound **1** (for clarity the water molecules and one of the diquaternary cations are not displayed) and (b) compound **4**. Positions of the bond and ring CPs are denoted by dark and light gray dots, respectively. The cage CP is labeled as ccp.

nickelate anion and one phenantroline diquaternary cation were included.

In both cases, besides the bond critical points (CP) in the charge density corresponding to the intramolecular bonds, several bond CPs appear connecting the anions and cations (Figure 5) and in compound **1** it is possible to find critical points corresponding to hydrogen bonds of the water molecules. The value of the charge density at all these intermolecular critical points is quite small ($\sim 10^{-3}$ au) and the Laplacian is small and positive, which is indicative of a closed-shell interaction and, in the particular case of these compounds, of $\pi - \pi$ interactions between the cyano groups of one of the $[Ni(CN)_4]^{2-}$ anions and the aromatic rings of the cations. In fact, the intermolecular atomic interaction lines connect CN nitrogen atoms to either an atom or a C−C bond CP of the aromatic rings. The properties of the charge density at the intermolecular CPs listed in Table 4.

To satisfy the Poincaré-Hopf relationship: $n - b + r - c = 1$ (where n is the number of nuclei and b, r, and c are the number of bond, ring, and cage CPs, respectively), five ring and one cage CPs appear between each anion and cation. As the bond CPs display a curvature of the charge density much smaller in the direction normal to the bond path than along it, the magnitude of the electron density at the ring and bond CPs is similar, which creates a region of almost constant electron density between the anion and cation (Figure 6).

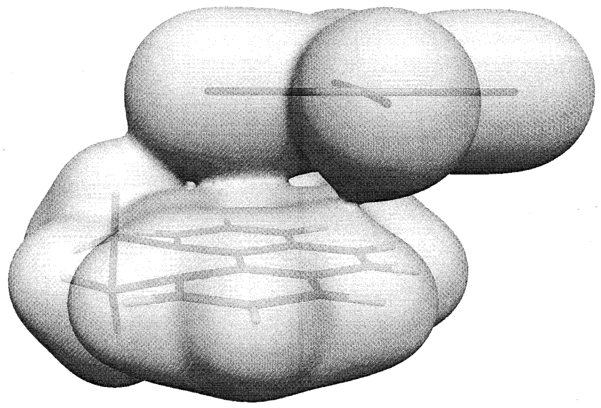

Figure 6. Display of an envelope of the electron density in compound **4** for a value equal to 0.0046 au, the minimum electron density at the intermolecular bond critical points.

Thermogravimetric Analysis. The thermogravimetric curves indicate that the thermal decompositions are not simple, because most of the stages are overlapped. This fact together with the great diversity of possible intermediate products preclude exhaustive interpretations and only the final inorganic degradation residues have been identified by X-ray powder diffraction techniques.

Thermal decomposition shows that compounds **1**−**3** are dihydrated, compound **4** is anhydrous, and compounds **5** and **6** are monohydrated.

The water molecules are lost between 50 and 105 °C during an endothermic step for compounds **1**, **2**, **5**, and **6**, and two steps for **3**. The anhydrous compounds are stable up to 240, 235, 275, 275, 250, and 300 °C, respectively.

The decomposition of these anhydrous compounds starts with an exothermic step followed by one progressive weight loss to give a residue that could contain a small amount of the corresponding metal fulminate,[13] whose presence may be guessed from the strongly exothermic character and abrupt weight loss of the next decomposition stage. This last stage gives stable residues at 405 (**1**), 450 (**2**), 460 (**3**), 365 (**4**), 384 (**5**), and 426 °C (**6**). In all cases, the final residue is a mixture of metal and metal oxide. In the case of compound **4** these three steps overlap. For the salts of the tetracyanopalladate anion, **2** and **5**, a progressive mass gain is observed above 450 °C, due to the oxidation of Pd to yield PdO.

Conclusions

Six new tetracyanometalate compounds of group 10 have been obtained from the reaction of aqueous solutions of the $[M(CN)_4]^{2-}$ anion and the $(C_{12}H_{12}N_2)^{2+}$ or $(C_{14}H_{12}N_2)^{2+}$ diquaternary cations. The three compounds of the bipyridinium diquaternary cation are dihydrated and isostructural. The compounds with the phenanthrolinium diquaternary cation present two different degrees of hydration: the nickel compound is anhydrous and the palladium and platinum compounds are monohydrated.

DFT calculations of the IR and Raman spectra present good agreement, in values and tendencies, with the experi-

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mental data. The agreement for the diquaternary cations is remarkable. The strong peaks between 2100 and 2200 cm^{-1}, associated with C≡N stretching vibrations, show a blue-shift when going from Ni to Pd, and less so from Pd to Pt. A strong blue-shift is also observed for the M−C stretching band, but in this case it is larger for the platinum compounds, as corroborated by the DFT calculations.

The diquaternary cation used determines the hydration degree and, consequently, the packing model of these compounds. Thus, all three bipyridinium derivatives are dihydrated and isostructural, showing a columnar structure that favors $\pi-\pi$ interactions between cyanide ligands of $[M(CN)_4]^{2-}$ anions and the aromatic rings of diquaternary cations. Meanwhile, the phenanthrolinium derivatives present different degrees of hydration depending on the metal atom. The nickel salt is anhydrous, and the palladium and platinum salts are monohydrated. The corresponding anhydrous salts present a gradual decrease of stability when going from nickel to platinum: both palladium and platinum monohydrated salts can be dehydrated at 125 °C, but the platinum salts rehydrate immediately.

The anhydrous salts show a bidimensional framework, which suggest the presence of $\pi-\pi$ interactions between cyanide ligands of $[M(CN)_4]^{2-}$ anions and the aromatic rings of diquaternary cations.

The DFT calculations performed on nickel compounds **1** and **4** demonstrate the presence of weak interactions between the cyano groups and the aromatic rings.

The most remarkable fact of the thermal behavior of these compounds is the abrupt and extremely exothermic nature of the last decomposition step (350−450 °C). The temperature range of this step gets narrower as the nobleness of metal increases and it is much narrower for the phenanthrolinium compounds than the bipyridinium compounds.

Experimental Section

General. Potassium tetracyanometalate(II) (M = Ni, Pd, and Pt), 2,2′-bipyridine, and 1,10-phenanthroline monohydrate were purchased as reagent grade and were used without further purification. The synthesis of 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinium dibromide, $(C_{12}H_{12}N_2)Br_2$,[14] and 5,6-dihydropyrazino[1,2,3,4-*lmn*]-1,10-phenanthrolinium dibromide, $(C_{14}H_{12}N_2)Br_2$,[9] was carried out according to literature methods. The content of water was determined thermogravimetrically (TG). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried on a Setaram Tag 24 S16 thermobalance under a 50 mL/min flow of synthetic air; the temperature was ramped from 20 to 600 °C at a rate of 5 deg/min. The infrared spectra were recorded on a Nicolet Magna FT-IR 550 spectrophotometer for KBr pellets in the 4000−400 cm^{-1} region. Raman spectra were recorded on a NICOLET 950 FT equipped with a laser Spectra Physics Nd: YVO_4 (1064 nm, 1.5 W). Carbon, nitrogen, and hydrogen were determined by organic microanalysis on a LECO CHNS 932 analyzer.

Synthesis. The complexes were prepared according to the following general procedure: To a well-stirred aqueous solution containing 1.10 mmol of $K_2[M(CN)_4]$ was added a 1.10 mmol aqueous solution of $(dq)Br_2\cdot H_2O$ at room temperature. Immediately, an insoluble microcrystalline powder was obtained. The resulting precipitate was filtered off, washed with water, acetone, and ethyl ether, and dried in air via suction. Approximately 85% yields were achieved for all complexes. The details of each particular synthesis are given below.

$(C_{12}H_{12}N_2)[Ni(CN)_4]\cdot 2H_2O$ (1). The yellow precipitate was recrystallized in cold water to give yellow needles suitable for single-crystal X-ray investigations. (Found: C, 50.60; H, 4.21; N, 21.81; $C_{16}H_{16}N_6NiO_2$ requires C, 50.17; H, 4.21; N, 21.94.)

$(C_{12}H_{12}N_2)[Pd(CN)_4]\cdot 2H_2O$ (2). The brown precipitate was recrystallized in cold water to give a polycrystalline material. (Found: C, 45.21; H 3.77; N 19.60; $C_{16}H_{16}N_6O_2Pd$ requires C, 44.61; H, 3.74; N, 19.51.)

$(C_{12}H_{12}N_2)[Pt(CN)_4]\cdot 2H_2O$ (3). The yellow precipitate was recrystallized in cold water to give yellow prismatic crystals suitable for X-ray investigations. (Found: C, 36.77; H 3.08; N 16.27; $C_{16}H_{16}N_6O_2Pt$ requires C, 37.00; H, 3.10; N, 16.18.)

$(C_{14}H_{12}N_2)[Ni(CN)_4]$ (4). The orange precipitate was recrystallized in cold water to give yellow-red crystals suitable for X-ray investigations. (Found: C, 58.28; H 3.16; N 22.36; $C_{18}H_{12}N_6Ni$ requires C, 58.27; H, 3.26; N, 22.65.)

$(C_{14}H_{12}N_2)[Pd(CN)_4]\cdot H_2O$ (5). The red-orange precipitate was recrystallized in cold water to give a polycrystalline material. (Found: C, 49.39; H 3.26; N 19.12; $C_{18}H_{14}N_6OPd$ requires C, 49.5; H, 3.23; N, 19.24.)

$(C_{14}H_{12}N_2)[Pt(CN)_4]\cdot H_2O$ (6). The red precipitate was recrystallized in cold water to give a polycrystalline material. Single crystals suitable for X-ray study were grown by slow diffusion of aqueous solutions of the reactives $(dq)Br_2\cdot H_2O$ and $K_2[Pt(CN)_4]$. (Found: C, 41.05; H 2.51; N 16.05; $C_{18}H_{14}N_6OPt$ requires C, 41.15; H, 2.69; N, 15.99.)

$(C_{14}H_{12}N_2)[Pd(CN)_4]$ (5b). A sample of 40 mg of compound **5** was dehydrated in the thermobalance, raising the temperature to 125 °C and keeping it there for 30 min to obtain a dark yellow powder.

$(C_{14}H_{12}N_2)[Pt(CN)_4]$ (6b). A sample of 16 mg of compound **6** was dehydrated in the thermobalance, raising the temperature to 125 °C and keeping it there for 15 min to obtain a dark yellow powder. This dehydrated compound is very unstable and rehydrates almost immediately, preventing any experimental characterization.

X-ray Diffraction Analysis. Single-crystal X-ray data collection for compounds **1**, **3**, **4**, and **6** was carried out at 293 K on a Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) and operating in the $\omega-2\theta$ scan mode. Unit cell parameters were determined from a least-squares fit of 25 well-centered reflections on the range $9 < \theta < 13$ for **1** and $7 < \theta < 14$ for **3**, $7 < \theta < 12$ for **4**, and $8 < \theta < 13$ for **6**. Intensities of two reflections monitored periodically exhibited no significant variation. The intensity data were corrected for Lorentz and polarization effects. Crystallographic details for all compounds are given in Table 5.

An empirical absorption correction was applied to data following the procedure DIFABS,[15] resulting in transmission factors ranging from 0.951 to 1.064 for **1**, 0.962 to 1.027 for **3**, 0.1546 to 0.8484 for **4**, and 0.0651 to 0.2894 for **6**. The atomic scattering factors for neutral atoms and anomalous dispersion corrections for non-hydrogen atoms were taken from the *International Tables for X-ray Crystallography*.[16]

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The structures were solved by a combination of Patterson and difference Fourier methods[17] and refined by full-matrix least-squares.[18] A convenient weighting scheme was used to obtain flat dependence in $\langle w\Delta^2F\rangle$ vs $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$.[19] In all compounds, non-hydrogen atoms were refined anisotropically.

Hydrogen atoms in compound **1** were located in a difference Fourier map and refined isotropically. For compound **3** the hydrogen atoms were introduced in the final refinement in calculated positions as fixed isotropic contributors ($U = 0.05$ Å^2).

For compounds **1** and **3** most calculations were carried out with the X-RAY76 System[20] running on a MicroVAX II computer and for compounds **4** and **6** the calculations were carried out with WINGX[21] running on a personal computer. Final atomic positional and thermal parameters, together with anisotropic thermal parameters for non-hydrogen atoms, a full list of bond distances and angles, dihedral angles, and a list of observed and calculated structure factors, have been deposited as Supporting Information. Atomic coordinates have also been submitted to the Cambridge Crystallographic Data Centre.

Compounds **2** and **5** crystallize in insufficient quality to be studied by X-ray single-crystal diffraction and powder X-ray diffraction has been performed to obtain structural information. The X-ray powder diffraction (XRD) patterns for compounds **2**, **5**, **5b**, and **6** were recorded on a STOE automatic diffractometer, equipped with germanium monochromated Cu Kα_1 radiation. An $\omega-2\theta$ scan was performed in the 2θ range $5 < 2\theta < 80°$ with increments of 0.02(2)° and a fixed-time counting of 12 s. Indexation of the diffraction profile and refinement of the cell parameters were made by FULLPROF (pattern-matching analysis)[8] on the basis of the space group and the cell parameters found for the isostructural compounds.

DFT Calculations. The geometry of the tetracyanometalate anions $[M(CN)_4]^{2-}$ in D_{4h} symmetry and diquaternary cations in C_{2v} symmetry was optimized starting from experimental values and their fundamental vibrations were calculated by using Density Functional Theory as implemented in the program Gaussian 98W.[22] Becke's three-parameter hybrid functional with the PW91 correlation functional[23] (B3PW91) was used in all calculations. The Los Alamos effective core potential combined with a DZ basis (LANL2DZ)[24] was chosen for the transition metals, as a compromise between accuracy and computational power available. For the remaining atoms, the 6-31G* basis[25] was used, supplemented with a set of diffuse functions in the case of the $[M(CN)_4]^{2-}$ anions.

The assignment of the calculated wavenumbers was aided by the animation option of the Molden 3.6[26] and MOLDRAW 1.0[27] programs that give a visual presentation of the shape of the vibrational modes.

The same theoretical level and basis sets were used to calculate the electron density in the systems, including a tetracyanonickelate anion sandwiched between two bipyridine diquaternary cations and seven water molecules for compound **1**, and the tetracyanonickelate anion and one phenantroline diquaternary cation for compound **4**. The location and properties of the critical points of the electron density were analyzed with AIM2000.[28]

Acknowledgment. This work was supported by MEC (Grant No. PB98/0238).

Supporting Information Available: Crystallographic data in CIF format for compounds **1**, **3**, **4**, and **6**; powder XRD data for compounds **2**, **5**, and **5b**; and graph of the correlation between the A_{1g} mode frequency and the value of the electron density at the M−C bond critical point. This material is available free of charge via the Internet at http://pubs.acs.org.

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