1372 *Inorg. Chem.* **2001,** *40,* 1372−1375

Syntheses and Characterization of the Metal Maleonitrilediselenolates $[K([2.2.2]\text{-cryptand})]_2[M(Se_2C_2(CN)_2)_2]$ (M = Ni, Pd, Pt) and $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$

Craig C. McLauchlan, Scott D. Robowski, and James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

Received August 1, 2000

Reaction of KNH_2, K_2Se, Se, [2.2.2]-cryptand, and a metal source yields the metal bis(maleonitrilediselenolates) $[K([2.2.2]\text{-cryptand})]_2[M(Se_2C_2(CN)_2)_2]$ (M = Ni, **1**; Pd, **2**, Pt, **3**). These compounds are isostructural and crystallize with four formula units in the monoclinic space group $P2_1/c$ in cells at $T = 153$ K with parameters (a (Å), b (Å), c (Å), β (deg), V (Å^3)) of 12.220(1), 15.860(2), 15.306(1), 107.64(2), 2827(1) for **1**; 12.291(1), 15.669(1), 15.548(1), 108.55(1), 2839(1) for **2**; and 12.292(3), 15.671(3), 15.569(3), 108.59(3), 2842(1) for **3**. The cation of **1** has been substituted to yield $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**4**). $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**4**) crystallizes with one molecule in the triclinic space group $P\bar{1}$ in a cell with parameters (T = 153 K) of a = 8.842(2) Å, b = 13.161(3) Å, c = 13.831(3) Å, α = 110.08(3)°, β = 95.23(3)°, γ = 93.72(3)°, V = 1484(1) Å^3. The electronic absorption and infrared spectra are characteristic of metal maleonitrilediselenolates. Cyclic voltammetry shows that the maleonitrilediselenolate (mns) complexes are more easily oxidized than their maleonitriledithiolate (mnt) analogues.

Introduction

Metal complexes containing the maleonitriledithiolate (mnt, $[S_2C_2(CN)_2]^{2-}$) ligand have been extensively studied. More specifically, metal bis(maleonitriledithiolate) complexes have received considerable attention owing to their use for charge transfer and storage and as molecular metals.[1−3] Despite the abundance of metal−mnt complexes and the extensive literature on $[Se_2C_2R_2]^{2-}$ species,[4−8] complexes of the selenium analogue of mnt, maleonitrilediselenolate (mns, $[Se_2C_2(CN)_2]^{2-}$), were unknown until recently. The first metal−mns complex was isolated as $[NBu_4]_2[Ni(mns)_2]$,[9] although unsuccessful earlier efforts are reported.[4] Recently we reported the syntheses of several metal−mns complexes, $[K([2.2.2]\text{-cryptand})]_3[Sb(mns)_2]$, $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$, $[K([2.2.2]\text{-cryptand})]_2[Ni(mns)_2]$ (**1**), and Ni(dppp)(mns), where dppp = 1,3-bis(diphenylphosphino)propane.[10,11] In our continuing work with the mns ligand, we report here the syntheses and characterization of a series of metal bis(maleonitrilediselenolate) complexes $[K([2.2.2]\text{-cryptand})]_2[M(Se_2C_2(CN)_2)_2]$ (M = Pd, **2** Pt, **3**) and $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**4**), as well as further characterization of $[K([2.2.2]\text{-cryptand})]_2[Ni(Se_2C_2(CN)_2)_2]$ (**1**).[11]

Experimental Section

All processes were carried out under N_2 with the use of standard Schlenk and air-free manipulation techniques. Se (99.9%), $AgBF_4$ (98%), $Pt(COD)Cl_2$ (COD = 1,5-cyclooctadiene) (99%), $Pd(dppe)Cl_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) (98%), $Ni(dppp)Cl_2$ (98%), $NiCl_2{\cdot}6H_2O$ (95%), and [2.2.2]-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) (98%) were purchased from Aldrich Chemicals, Milwaukee, WI, and used without further purification. K_2Se was prepared by the stoichiometric combination of the elements in liquid ammonia. KNH_2 was prepared by reaction of KH with liquid ammonia. $[K([2.2.2]\text{-cryptand})]_3[Ag(Se_2C_2(CN)_2)(Se_6)]$ was prepared by a published method.[11] *N*,*N*-Dimethylformamide (dmf) was dried over 4A sieves and deoxygenated prior to use. All other solvents were dried and distilled prior to use. Electronic absorption spectra were collected on a Bio-Rad Digilab FTS-60 FTIR as KBr mulls. UV−visible spectra were collected on a Cary 1E UV−visible spectrophotometer. Electrospray mass spectroscopic analyses were performed on a Micromass Quatro II triple quadrupole instrument operated in negative ion mode. Energy dispersive spectroscopy was performed on an EDS equipped Hitachi S-4500 field emission scanning electron microscope. Cyclic voltammetry studies were performed at 5 mM in 0.1 M solutions of $[NBu_4][PF_6]$ in acetonitrile on a Princeton Applied Research bipotentiostat with a Ag/AgCl reference electrode. Melting point determinations were performed with a Mel-Temp device on samples in glass capillaries. Microanalyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of $[K([2.2.2]\text{-cryptand})]_2[Ni(Se_2C_2(CN)_2)_2]$ (1). This compound was prepared according to the literature method.[11]

Preparation of $[K([2.2.2]\text{-cryptand})]_2[Pd(Se_2C_2(CN)_2)_2]$ (2). A mixture of 11 mg (0.2 mmol) of KNH_2, 63 mg (0.4 mmol) of K_2Se, 158 mg (2 mmol) of Se, 340 mg (0.9 mmol) of [2.2.2]-cryptand, and 40 mg (0.2 mmol) of $Pd(dppe)Cl_2$ was dissolved in 10 mL of acetonitrile. The flask containing the resultant green solution was wrapped in foil to keep out light. After it was stirred for 24 h, the solution was filtered and the red-green filtrate was cooled to 4 °C and then layered with 11 mL of diethyl ether/toluene (10:1). $Pd(PhCN)_2Cl_2$ may be substituted for $Pd(dppe)Cl_2$. After 7 d red crystals of **2** were isolated cocrystallized with what we believe is a $[K([2.2.2]\text{-cryptand})]_2[Pd(Se_2C_2(CN)_2)(Se_4)]$ impurity. Recrystallization did not improve the purity. From the refinement of X-ray diffraction data from a single

---

(1) Bähr, G.; Schleitzer, G. *Chem. Ber.* **1955**, *88*, 1771−1777.
(2) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49−221.
(3) Clemenson, P. I. *Coord. Chem. Rev.* **1990**, *106*, 171−203.
(4) Davison, A.; Shawl, E. T. *Inorg. Chem.* **1970**, *9*, 1820−1825.
(5) Nigrey, P. J. *Synth. React. Inorg. Met.−Org. Chem.* **1986**, *16*, 1351−1355.
(6) Olk, B.; Olk, R.-M.; Sieler, J.; Hoyer, E. *Synth. Met.* **1991**, *41−43*, 2585−2588.
(7) Olk, R.-M.; Röhr, A.; Olk, B.; Hoyer, E. *Z. Chem.* **1988**, *8*, 304−305.
(8) Dietzsch, W.; Franke, A.; Hoyer, E.; Gruss, D.; Hummel, H.-U.; Otto, P. *Z. Anorg. Allg. Chem.* **1992**, *611*, 81−84.
(9) Morgado, J.; Santos, I. C.; Duarte, M. T.; Alcácer, L.; Almeida, M. *J. Chem. Soc., Chem. Commun.* **1996**, 1837−1838.
(10) Smith, D. M.; Albrecht-Schmitt, T. E.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1089−1091.
(11) McLauchlan, C. C.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 1046−1048.

10.1021/ic0008666 CCC: $20.00

Table 1. Crystallographic Data for [K([2.2.2]-cryptand)]$_2$[Pd(Se$_2$C$_2$(CN)$_2$)$_2$]^a (**2**), [K([2.2.2]-cryptand)]$_2$[Pt(Se$_2$C$_2$(CN)$_2$)$_2$] (**3**), and [Ni(dmf)$_5$Cl]$_2$[Ni(Se$_2$C$_2$(CN)$_2$)$_2$] (**4**)

	2	**3**	**4**
chemical formula	$C_{44}H_{72}K_2N_8PdO_{12}Se_4$^{a}	$C_{44}H_{72}K_2N_8PtO_{12}Se_4$	$C_{38}H_{70}Cl_2N_{12}Ni_3O_{10}Se_4$
fw	1405.54^a	1494.23	1445.95
a (Å)	12.291(1)	12.292(3)	8.842(2)
b (Å)	15.669(1)	15.671(3)	13.161(3)
c (Å)	15.548(1)	15.569(3)	13.831(3)
α (deg)	90	90	110.08(3)
β (deg)	108.55(1)	108.59(3)	95.23(3)
γ (deg)	90	90	93.72(3)
V (Å^3)	2839(1)	2842(1)	1498(1)
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	2	2	1
ρ_{calcd} (g cm^{-3})	1.645^a	1.746	1.603
λ (Å)	0.710 73	0.710 73	0.710 73
μ (cm^{-1})	31.00^a	52.38	35.12
temp (K)	153(2)	153(2)	153(2)
R_1 (F_o)^b	0.044	0.039	0.028
wR_2 (F_o^2)^c	0.085	0.081	0.063

[a] The formulation for **2** admixed with [K([2.2.2]-cryptand)]$_2$[Pd(Se$_2$C$_2$(CN)$_2$)(Se$_4$)], as derived from the crystallographic data, is [K([2.2.2]-cryptand)]$_2$[Pd(Se$_2$C$_2$(CN)$_2$)$_{1.76}$(Se$_4$)$_{0.24}$]. However, ρ, fw, and μ are tabulated for the formula [K([2.2.2]-cryptand)]$_2$[Pd(Se$_2$C$_2$(CN)$_2$)$_2$]. [b] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.03F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

crystal (see below) the resultant formulation is [K([2.2.2]-cryptand)]$_2$[Pd(Se$_2$C$_2$(CN)$_2$)$_{1.76}$(Se$_4$)$_{0.24}$]. Bulk analyses from several preparations give a higher Se content than this formulation. Yield: 12 mg (5% based on Pd(dppe)Cl$_2$). UV−vis (CH$_2$Cl$_2$) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 351 (6600), 437 (3600), 523 (900). IR (ν, CN region, cm^{-1}): 2185, 2192, 2210. ESI (−): 575.4 (m/z, [HPd(Se$_2$C$_2$(CN)$_2$)$_2$]$^-$), 341.6 (m/z, [Pd(Se$_2$C$_2$(CN)$_2$)]$^-$), 287.5 (m/z, Pd([Se$_2$C$_2$(CN)$_2$)$_2$]$^{2-}$). EDS: K/Pd/Se, 1.7:1:4.6. Mp: 240−242 °C.

Preparation of [K([2.2.2]-cryptand)]$_2$[Pt(Se$_2$C$_2$(CN)$_2$)$_2$] (3). A mixture of 11 mg (0.2 mmol) of KNH$_2$, 63 mg (0.4 mmol) of K$_2$Se, 158 mg (2 mmol) of Se, and 340 mg (0.9 mmol) of [2.2.2]-cryptand was dissolved in 10 mL of acetonitrile. Another flask was charged with 17 mg (45 mmol) of Pt(COD)Cl$_2$ and 2 mL of dmf. After 10 min the clear, colorless Pt solution was added dropwise to the green selenide solution. After it was stirred for 48 h, the resultant solution was filtered and the red-green filtrate was cooled to 4 °C and then layered with 11 mL of diethyl ether/toluene (10:1). Red crystals of **3** were isolated after 7 d. Yield: 29 mg (43% based on Pt(COD)Cl$_2$). UV−vis (CH$_2$Cl$_2$) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 243 (16700), 370 (5000), 470 (1600). IR (ν, CN region, cm^{-1}): 2183, 2190, 2202. EDS: K/Pt/Se, 2.1:1:4.3. Anal. Calcd for $C_{44}H_{72}K_2N_8PtO_{12}Se_4$: C, 35.37; H, 4.86; N, 7.50. Found: C, 34.11; H, 4.74; N, 6.54. $E_{1/2}$ (V): 0.272. Mp: 236−240 °C.

Preparation of [Ni(dmf)$_5$Cl]$_2$[Ni(Se$_2$C$_2$(CN)$_2$)$_2$] (4). A mixture of 8 mg (4 μmol) of [K([2.2.2]-cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)(Se$_6$)] and 10 mg (42 μmol) of NiCl$_2$·6H$_2$O was dissolved in 3 mL of water. After it was stirred for 12 h, the colorless solution was removed and the resultant precipitate dried in vacuo. The precipitate was dissolved in 3 mL of dmf, and the resultant red solution was stirred for 1 h, filtered, and layered with 5 mL of diethyl ether/toluene (10:1). Red crystals of **4** were isolated in very low yield after 2 d. Crystals of **4** effloresce rapidly upon being removed from their mother liquor. UV−vis (MeCN) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 332 (4200), 410 (1400), 433 (1100). IR (ν, CN region, cm^{-1}): 2170. EDS: Cl/Ni/Se, 1.94:3:3.77.

Crystallography. A crystal of compound **2**, **3**, or **4** was mounted on the end of a fiber on a goniometer head that was then placed in the cold stream of a Bruker-AXS SMART-1000 diffractometer equipped with a CCD area detector and graphite monochromated Mo Kα radiation. Data were collected at 153 K at 0.3° steps in ω for 606 frames each at $\varphi = 0°$, 120°, and 240° and another 50 frames at $\varphi = 0°$. Data were processed with the program SAINT+,[12] and a face-indexed absorption correction was calculated with the program XPREP of the SHELXTL-98 suite.[13] Data were further corrected for frame variations with the program SADABS,[12] which relies on redundancy in the data. Structure solutions were found by direct methods and refined on F^2 with the use of full-matrix least-squares techniques.[13] Refinement of the structures of compounds **3** and **4** was straightforward, but there were complications in the refinement of compound **2** in that some atoms of the mns ligand did not refine well and chemically unreasonable distances resulted. There must be another component present in addition to the mns ligand. [K([2.2.2]-cryptand)]$_2$[Pd(Se$_4$)$_2$][14] crystallizes in the triclinic space group $P\bar{1}$, so it is unlikely that cocrystallization of it and [K([2.2.2]-cryptand)]$_2$[Pd(mns)$_2$] ($P2_1/c$) has occurred. X-ray powder diffraction patterns of **2** show peaks in addition to those calculated for [K([2.2.2]-cryptand)]$_2$[Pd(mns)$_2$], but these peaks do not correspond to those of [K([2.2.2]-cryptand)]$_2$[Pd(Se$_4$)$_2$]. Mass spectrometry experiments show the presence of the [Pd(mns)]$^-$ and [Pd(mns)$_2$]$^{2-}$ species but not the [Pd(Se$_4$)$_2$]$^{2-}$, [Pd(Se$_4$)]$^-$, or [Pd(mns)(Se$_4$)]$^{2-}$ species. After a variety of models were conjured up and found to be unsatisfactory, we settled on one in which the major anionic component [Pd(mns)$_2$]$^{2-}$ is contaminated with the minor anionic component [Pd(mns)(Se$_4$)]$^{2-}$. The occupancies of the two ligand systems were refined in space group $P2_1/c$ and led to the ratio [K([2.2.2]-cryptand)]$_2$[Pd(mns)$_2$]/[K([2.2.2]-cryptand)]$_2$[Pd(mns)(Se$_4$)] = 0.759:0.241 and to the resultant formulation $C_{43.04}H_{72}K_2N_{7.52}PdO_{12}Se_{4.48}$. The model is not totally satisfactory, and some displacement ellipsoids remain unreasonably large. Crystallographic details for all three structures are summarized in Table 1 and in Supporting Information.

Results and Discussion

Syntheses. Reaction of KNH$_2$, K$_2$Se, Se, [2.2.2]-cryptand, and a metal source (M = Ni,[11] Pd, Pt) in acetonitrile yields [K([2.2.2]-cryptand)]$_2$[M(Se$_2$C$_2$(CN)$_2$)$_2$] (M = Ni **1**, Pd **2**, Pt **3**). Reaction of [K([2.2.2]-cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)(Se$_6$)] with NiCl$_2$·6H$_2$O in water followed by dissolution in and crystallization from dmf yields the complex [Ni(dmf)$_5$Cl]$_2$[Ni(Se$_2$C$_2$(CN)$_2$)$_2$] (**4**). The unusual [Ni(dmf)$_5$Cl]$^+$ cation probably results from the large excess of NiCl$_2$·6H$_2$O used in the synthesis because the related [Ni(dmf)$_6$]$^{2+}$ cation results when a large excess of Ni(ClO$_4$)$_2$[15] or Ni(BF$_4$)$_2$[16] was used under similar conditions.

---

[12] *SMART* Data Collection, version 5.054; *SAINT-Plus* Data Processing Software for the *SMART* System, version 6.02A; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 2000.

[13] Sheldrick, G. M. *SHELXTL* DOS/Windows/NT, version 5.10; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 1997.

[14] McLauchlan, C. C.; Ibers, J. A. Unpublished results.

[15] McKee, V.; Metcalfe, T.; Wikaira, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 1139−1141.

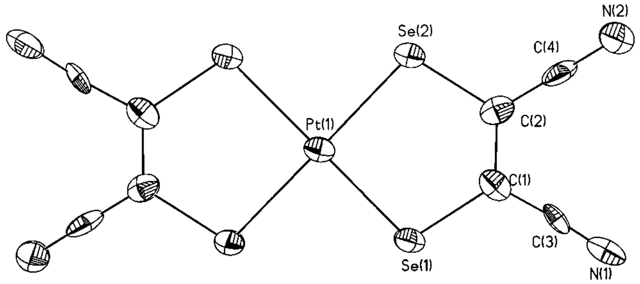

Figure 1. Drawing of the $[Pt(mns)_2]^{2-}$ anion in $[K([2.2.2]\text{-cryptand})]_2[Pt(Se_2C_2(CN)_2)_2]$ (**3**). The anion possesses a crystallographically imposed center of symmetry. Displacement ellipsoids are drawn here and in Figure 2 at the 50% probability level.

Table 2. Average^a Bond Distances (Å) and Bond Angles (deg) in $[M(mns)_2]^{2-}$ Complexes

	Ni(**1**)^b	Pd(**2**)^c	Pt(**3**)^d	Ni(**4**)^e	Ni^f
M−Se	2.292(1)	2.4022(5)	2.4005(9)	2.2890(7)	2.285
Se−C	1.874(4)	1.872(5)	1.892(4)	1.888(2)	1.876
C=C	1.350(5)	1.366(6)	1.393(6)	1.343(3)	1.357
C−CN	1.439(6)	1.49(2)	1.331(6)	1.435(3)	1.422
C−N	1.136(5)	1.053(18)	1.164(6)	1.138(3)	not reported
Se−M−Se	93.17(2)	91.61(2)	91.42(3)	92.99(3)	92.8
M−Se−C	101.3(1)	100.3(2)	101.5(1)	101.60(8)	102.1
Se−C=C	121.9(3)	119.6(6)	122.7(3)	121.6(2)	121.4
C=C−CN	121.3(4)	123.7(4)	120.2(3)	121.2(2)	121.4
C−C−N	178.9(5)	177.9(19)	176.8(5)	179.6(3)	178.3

[a] Average values are unweighted arithmetic means with the largest esd of the series as the esd. [b] $[K([2.2.2]\text{-cryptand})]_2[Ni(Se_2C_2(CN)_2)_2]$, ref 11. [c] $[K([2.2.2]\text{-cryptand})]_2[Pd(Se_2C_2(CN)_2)_2]$ (**2**), this work. [d] $[K([2.2.2]\text{-cryptand})]_2[Pt(Se_2C_2(CN)_2)_2]$ (**3**), this work. [e] $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**4**), this work. [f] $[NBu_4]_4[Ni(mns)_2]$, ref 9.

Table 3. Average^a Bond Distances (Å) and Bond Angles (deg) in the $[Ni(dmf)_5Cl]^+$ Cation of $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**4**)

Ni−O	2.063(2)	cis O−Ni−O	87.97(7)
Ni−Cl	2.380(1)	cis O−Ni−Cl	93.94(5)
O=C	1.240(3)	C=O−Ni	124.4(2)
$C-N(CH_3)_2$	1.323(3)	$O=C-N(CH_3)_2$	124.0(2)
H_3C-N	1.455(3)	$H_3C-N-CH_3$	117.4(2)

[a] Average values are unweighted arithmetic means with the largest esd of the series as the esd.

Structures. The crystal structures of $[K([2.2.2]\text{-cryptand})]_2[M(Se_2C_2(CN)_2)_2]$ (M = Ni,[11] Pd, Pt) and $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**1**−**4**) all possess well-separated anions and cations. In all four complexes, the square-planar $[M(mns)_2]^{2-}$ anion possesses a crystallographically imposed center of symmetry. The anion in each case is essentially planar. A drawing of the M = Pt anion is shown in Figure 1. Selected bond distances and angles for compounds **1**−**4** are summarized in Table 2.

Compound **4**, $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$, possesses the unusual $[Ni(dmf)_5Cl]^+$ cation (Figure 2) in which the octahedrally coordinated Ni center has bond lengths and angles akin to those found in the $[Ni(dmf)_6]^{2+}$ cation.[15,16] Average bond distances for the $[Ni(dmf)_5Cl]^+$ cation of **4** are summarized in Table 3.

Spectroscopy. The CN region of the infrared spectrum is similar in compounds **1**−**3** (Figure 3) and is consistent with the CN regions of the spectra of other known mns complexes,[10,11] including compound **4**. Note that the infrared spectrum of **2** is unaffected by the mns/Se_4^{2-} disorder because Se_4^{2-} is transparent in the region of interest.

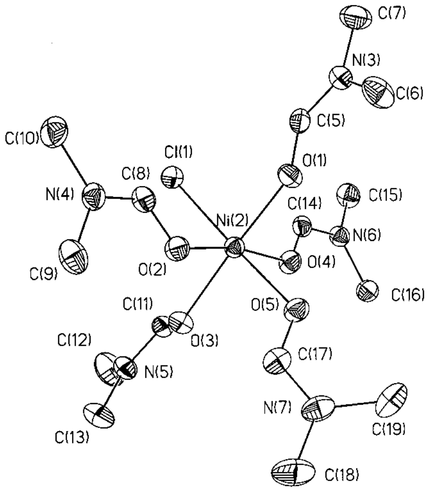

Figure 2. Drawing of the $[Ni(dmf)_5Cl]^+$ cation of $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**4**). Hydrogen atoms have been omitted for the sake of clarity.

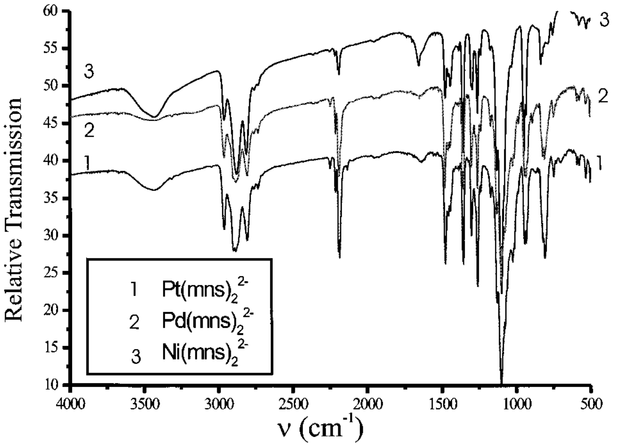

Figure 3. Infrared spectra of $[M(mns)_2]^{2-}$ (M = Ni, Pd, Pt).

Electronic (UV−vis) absorptions, however, do vary among the complexes. $[K([2.2.2]\text{-cryptand})]_2[Ni(Se_2C_2(CN)_2)_2]$ (**1**) shows absorptions at 281, 331, 399, and 495 nm,[11] and $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**4**) shows absorptions at 332, 410, and 433 nm. These spectra are dominated by a peak (∼331 nm) that has been assigned to ligand-to-metal charge transfer (LMCT) in the analogous mnt complexes.[17] Not surprisingly then, slight variations are seen in $[K([2.2.2]\text{-cryptand})]_2[Pd(Se_2C_2(CN)_2)_2]$ (**2**) and $[K([2.2.2]\text{-cryptand})]_2[Pt(Se_2C_2(CN)_2)_2]$ (**3**) where absorptions occur at 351, 437, and 523 nm and 243, 370, and 470 nm, respectively. Extended Hückel calculations on $[M(mns)_2]^{2-}$ complexes indicate that the ligand−metal overlap is the lowest unoccupied molecular orbital that would support the LMCT assignment.[18] Similar results are noted in the mnt analogues.[17]

Cyclic Voltammetry. Cyclic voltammetry data are given for complexes **1** and **3** as well as for their mnt analogues $[Ni(mnt)_2]^{2-}$ and $[Pt(mnt)_2]^{2-}$ in Table 4. The trends for Ni vs Pt are the same in both systems; the mns species are more easily oxidized than their mnt analogues.

---

(16) Li, W.-S.; Blake, A. J.; Champness, N. R.; Schröder, M.; Bruce, D. W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, *54*, 349−351.

(17) Shupack, S. I.; Billig, E.; Clark, R. J. H.; Williams, R.; Gray, H. B. *J. Am. Chem. Soc.* **1964**, *86*, 4594−4602.

(18) Huang, F. Q.; McLauchlan, C. C.; Ibers, J. A. Unpublished results.

(19) Davison, A.; Holm, R. H. *Inorg. Synth.* **1967**, *10*, 8−26.

Table 4. First Oxidation Potentials of $[M(mns)_2]^{2-}$ and $[M(mnt)_2]^{2-}$ Complexes

	oxidation potential[a] (V)	reported oxidation potential (V)
$[Ni(mns)_2]^{2-}$ (**1**) $\rightleftarrows$ $[Ni(mns)_2]^-$	0.310	
$[Pt(mns)_2]^{2-}$ (**3**) $\rightleftarrows$ $[Pt(mns)_2]^-$	0.272	
$[Ni(mnt)_2]^{2-}$ [b] $\rightleftarrows$ $[Ni(mnt)_2]^-$	0.271	0.23[c]
$[Pt(mnt)_2]^{2-}$ [b] $\rightleftarrows$ $[Pt(mnt)_2]^-$	0.259	0.21[c]

[a] $E_{1/2}$ values reported vs Ag/AgCl. [b] $[NBu_4]_2[Ni(mnt)_2]$ and $[NEt_4]_2[Pt(mnt)_2]$ were prepared according to ref 19. [c] Reported values were obtained in acetonitrile vs SCE; ref 2.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-9819385). The authors thank Dennis A. Gaal for assistance with CV studies. S.D.R. acknowledges the support of the Research Experience for Science Teachers program within the MRSEC program of the National Science Foundation (Grant DMR-9632472) at the Materials Research Center of Northwestern University. The mass spectrometer was purchased with a grant from the National Institutes of Health (Grant S10 RR11320).

Supporting Information Available: Crystallographic data for $[K([2.2.2]\text{-cryptand})]_2[Pd(Se_2C_2(CN)_2)_{1.76}(Se_4)_{0.24}]$ (**2**), $[K([2.2.2]\text{-cryptand})]_2[Pt(Se_2C_2(CN)_2)_2]$ (**3**), and $[Ni(dmf)_5Cl]_2[Ni(Se_2C_2(CN)_2)_2]$ (**4**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0008666