1046 *Inorg. Chem.* **2000,** *39,* 1046−1048

Facile Syntheses and Structures of New Metal−Maleonitrilediselenolates [K([2.2.2]-cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)(Se$_6$)], [K([2.2.2]-cryptand)]$_2$[Ni(Se$_2$C$_2$(CN)$_2$)$_2$], and Ni(dppp)(Se$_2$C$_2$(CN)$_2$)

Craig C. McLauchlan and James A. Ibers*

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

Received February 10, 1999

Introduction

Metal complexes containing the maleonitriledithiolate (mnt, [S$_2$C$_2$(CN)$_2$)]$^{2-}$) ligand have been extensively studied. The literature abounds with uses of metal−mnt complexes for charge transfer, for charge storage, and as molecular metals.[1−3] Despite the abundance of metal−mnt complexes and the extensive literature on [Se$_2$C$_2$R$_2$]$^{2-}$ species,[4−8] complexes of the selenium analogue of mnt, maleonitrilediselenolate (mns, [Se$_2$C$_2$(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] The [Ni(mns)$_2$]$^{2-}$ species was isolated by a difficult synthesis involving carbon diselenide and dicyanoacetylene.[9] Recently, we reported the serendipitous syntheses of two metal−mns complexes, [K([2.2.2]-cryptand)]$_3$[Sb(mns)$_2$] and [K([2.2.2]-cryptand)]$_3$[Ag(mns)(Se$_6$)] (**1**).[10] We report here an improved synthesis of complex **1** and the syntheses of [K([2.2.2]-cryptand)]$_2$[Ni(Se$_2$C$_2$(CN)$_2$)$_2$] (**2**) and Ni(dppp)(Se$_2$C$_2$(CN)$_2$) (**3**), where dppp = 1,3-bis(diphenylphosphino)propane.

Experimental Section

General Procedures. Infrared spectra were collected on a Bio-Rad Digilab FTS-60 FTIR spectrometer for samples as KBr mulls. ^{1}H and ^{31}P NMR spectra were collected on a Gemini 300 instrument; ^{31}P NMR spectra were referenced to neat H$_3$PO$_4$. K$_2$Se was prepared stoichiometrically from the elements in liquid ammonia. KNH$_2$ was prepared by reaction of KH with liquid ammonia. Ni(dppp)Cl$_2$ (97%), Se (99.9%), AgBF$_4$ (98%), and [2.2.2]-cryptand (=4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (98%) were purchased commercially and were used without further purification. *N,N*-dimethylformamide (dmf) was dried over 4 Å sieves and degassed prior to use. Electrospray mass spectroscopic analyses were performed on a Microscan Quattro II instrument operated in a positive ion mode. Energy dispersive spectroscopy was performed on an EDAX equipped Hitachi S-4500 field emission scanning electron microscope. Microanalyses were performed by Oneida Research Services, Whitesboro, NY.

X-ray Structure Determinations. Intensity data were collected at −120 °C on a Bruker AXS SMART-1000 diffractometer equipped with a CCD area detector. Graphite monochromatized Mo Kα radiation was used. Structures were solved by means of direct methods and were refined on F^2 with the use of full-matrix least-squares techniques.[11] The crystallographic results are summarized in Table 1. Further details are provided in Supporting Information.

Synthesis of [K([2.2.2]-cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)(Se$_6$)] (1). A mixture of 5.6 mg (0.1 mmol) of KNH$_2$, 40 mg (0.2 mmol) of AgBF$_4$, 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; a green solution resulted. The reaction flask was wrapped in aluminum foil to keep out light. After 20 h the solution was filtered and the green filtrate was cooled to 4 °C and kept there for 1−3 h. The filtrate was layered with 10 mL of diethyl ether/toluene (10:1), and dark red crystals of **1** were isolated after 48 h. Yield: 0.164 g (40% based on Ag). Reaction with AgCl in lieu of AgBF$_4$ yields the same product.

Synthesis of [K([2.2.2]-cryptand)]$_2$[Ni(Se$_2$C$_2$(CN)$_2$)$_2$] (2). For method 1, 15 mg (7.2 μmol) of **1** was dissolved in 5 mL of dmf to afford a brown solution. NiCl$_2$ (0.4 mg, 3.2 μmol) was suspended in 2 mL of dmf. After 1 h the NiCl$_2$ suspension was added to the solution of [K([2.2.2]-cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)(Se$_6$)] (**1**) to give a lighter brown solution. After 4 h this solution was filtered to remove Se, and the resultant orange filtrate was reduced 70% in volume in vacuo. The resultant solution was layered with 7 mL of diethyl ether/toluene (10:1), and red plates of **2** were isolated after 24 h. Yield: 5 mg (50% on **1**)

For method 2, a mixture of 11 mg (0.2 mmol) of KNH$_2$, 63 mg (0.4 mmol) of K$_2$Se, 158 mg of Se (2 mmol), and 340 mg (0.9 mmol) of [2.2.2]-cryptand was dissolved in 10 mL of acetonitrile to give a green solution. Ni(dppp)Cl$_2$ (55 mg, 0.1 mmol) was dissolved in 5 mL of acetonitrile. After 1 h the Ni(dppp)Cl$_2$ solution was added to the first solution; a green solution resulted. After 14 h the solution was filtered and the green filtrate was cooled to 4 °C for 1−3 h. The filtrate was layered with 11 mL of diethyl ether/toluene (10:1), and dark red crystals of **2** were isolated after 48 h. Yield: 0.148 g (54% on Ni). IR (KBr) (CN region, cm^{-1}): 2187. UV/vis (dmf (nm, ϵ)): 281 (6695), 331 (5237), 399 (2376), 495 (1264). Anal. Calcd for C$_{44}$H$_{72}$K$_2$N$_8$NiO$_{12}$Se$_4$: C, 38.92; H, 5.34; N, 8.25. Found: C, 38.42; H, 5.08; N, 7.75. ^{31}P NMR spectrum of the reaction mixture of method 2 in CH$_3$CN spiked with CD$_3$CN: −18.3 ppm.

Synthesis of Ni(dppp)(Se$_2$C$_2$(CN)$_2$) (3). An amount of 10 mg (4.8 μmol) of [K([2.2.2]-cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)(Se$_6$)] (**1**) was dissolved in 5 mL of dmf to give a brown solution. An orange solution was obtained when Ni(dppp)Cl$_2$ (9 mg, 18.0 μmol) was dissolved in 2 mL of dmf. After being stirred for 1 h, the Ni(dppp)Cl$_2$ solution was added to the solution of **1**. After 4 h the solution was filtered to remove Se and the resultant filtrate was reduced to dryness in vacuo. The residue was redissolved in a minimum of dmf (~2 mL) and layered with 5 mL of diethyl ether/toluene (10:1). Orange needles were isolated after 48 h. Yield: 0.15 mg (4% on **1**). Mp, 119 °C. IR (KBr) (CN region, cm^{-1}): 2204. UV/vis (CH$_2$Cl$_2$ (nm, ϵ)): 271 (5700), 285 (6734), 301 (5211), 331 (1764), 392 (638), 578 (82). ^{1}H NMR (CD$_2$Cl$_2$, ppm, 300 MHz) δ 2.41 (dt, 4H, CH$_2$), 2.79 (m, 2H, CH$_2$), 7.10 (dd, 8H, Ar−H), 7.46(d, 8H, Ar−H), 7.76(t, 4H, Ar−H). ESI MS(+): 678.9 (m/z, (Ni(dppp)(Se$_2$C$_2$CN))$^+$). EDS shows consistent ratios of 2:1:2 for P/Ni/Se for C$_{31}$H$_{26}$N$_2$NiP$_2$Se$_2$ (**3**).

Results and Discussion

Previously, we reported that addition of [Ir(cod)Cl]$_2$ (cod = 1,5-cyclooctadiene) to AgBF$_4$, K$_2$Se, Se, and [2.2.2]-cryptand in liquid ammonia followed by evaporation of the ammonia and dissolution of the residue in acetonitrile yielded [K([2.2.2]-

---

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

10.1021/ic9901719 CCC: $19.00 © 2000 American Chemical Society
Published on Web 02/02/2000

Table 1. Crystallographic Data for $[K([2.2.2]\text{-cryptand})]_2[Ni(Se_2C_2(CN)_2)_2]$ (**2**) and $Ni(dppp)(Se_2C_2(CN)_2)$ (**3**)

compound	**2**	**3**
chemical formula	$C_{44}H_{72}K_2N_8NiO_{12}Se_4$	$C_{31}H_{26}N_2NiP_2Se_2$
fw	1357.85	705.11
a, Å	12.220(1)	12.400(1)
b, Å	15.860(2)	15.407(1)
c, Å	15.306(1)	14.451(1)
β, deg	107.64(2)	90
V, Å^3	2827(1)	2952(1)
space group	$P2_1/c$	*Pnma*
Z	2	4
λ, Å	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	1595	1587
μ, cm^{-1}	313	326
T, K	153(2)	153(2)
$R_1(\mathbf{F})^a$	0.044	0.026
$wR2(F_o^2)^b$	0.081	0.059

[a] $R_1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.03F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 = 0$.

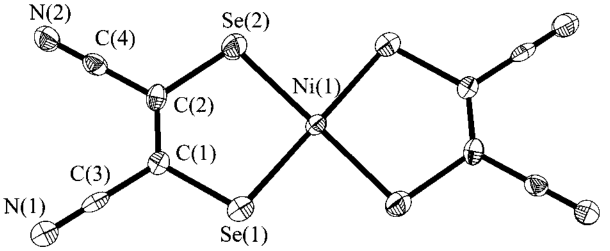

Figure 1. Structure of the anion in **2**, $[Ni(Se_2C_2(CN)_2)_2]^{2-}$. Here and in Figure 2 displacement ellipsoids are drawn at the 50% probability level.

cryptand)]$_3$[Ag(Se$_2$C$_2$(CN)$_2$)(Se$_6$)] (**1**).[10] A more direct synthesis has been devised in which a mixture of $AgBF_4$, K_2Se, Se, [2.2.2]-cryptand, and KNH_2 in acetonitrile affords complex **1**. This route leads to higher yields (40% vs 16%) and avoids the use of both the relatively costly Ir starting material and of liquid ammonia as a solvent.

$$4''\{K\}_2Se_4'' + \{K\}[NH_2] + 2AgBF_4 \xrightarrow[\text{2. Et}_2\text{O/toluene}]{\text{1. MeCN}} \{K\}_3[Ag(mns)(Se_6)] \quad (1)$$

$\{K\} = [K([2.2.2]\text{-cryptand})]$

The addition of $NiCl_2$ to complex **1** in dmf affords red crystals of $[K([2.2.2]\text{-cryptand})]_2[Ni(Se_2C_2(CN)_2)_2]$ (**2**) and gray Se. Complex **2** can also be formed under conditions similar to those used to make complex **1**. Complex **2** can be made directly in 54% yield by reaction of KNH_2, K_2Se, Se, and [2.2.2]-cryptand with Ni(dppp)Cl$_2$ in acetonitrile. In this reaction the mns ligand displaces the chloro and dppp ligands. The presence of free dppp in solution was confirmed by a ^{31}P NMR spectrum. But the addition of Ni(dppp)Cl$_2$ to complex **1** in dmf affords orange needles of $Ni(dppp)(Se_2C_2(CN)_2)$ (**3**), $[K([2.2.2]\text{-cryptand})]_2[NiCl_4]$, and gray Se.

$[K([2.2.2]\text{-cryptand})]_2[Ni(Se_2C_2(CN)_2)_2]$ (**2**) possesses well-separated anions and cations. The $[Ni(mns)_2]^{2-}$ anion of **2** is depicted in Figure 1. This anion, which is similar to that in $[NBu_4]_2[Ni(mns)_2]$,[9] comprises a square-planar Ni center coordinated by two mns ligands. Since a square-planar environment is that expected for Ni(II) and since the overall charge on the anion is −2, we assign a formal charge of −2 to the mns ligand. The "noninnocence" of mnt, however, is well documented,[2,3,12] and mns is expected to behave similarly. The molecule $Ni(dppp)(Se_2C_2(CN)_2)$ (**3**) (Figure 2) has a square-planar Ni(II) center coordinated by the bidentate dppp ligand and a single mns ligand. Table 2 shows average bond lengths within the mns ligand for the known metal−mns complexes.

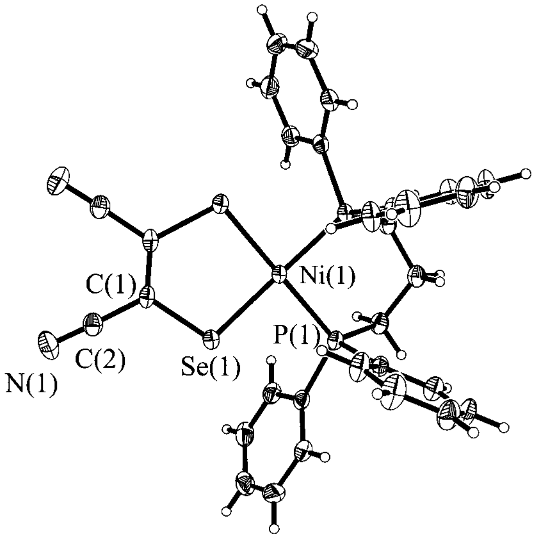

Figure 2. Structure of **3**, $Ni(dppp)(Se_2C_2(CN)_2)$. Hydrogen atoms are drawn as arbitrarily small circles. The molecule has a crystallographically imposed mirror plane.

Table 2. Average Bond Distances (Å) and Bond Angles (deg) in Metal−mns Complexes

	Ni^a	Ni (**2**)^b	Ni (**3**)^b	Sb^c	Ag (**1**)^c
			Bond Distances		
M−Se	2.285	2.292(1)	2.285(1)	2.654(2)	2.567(4)
Se−C	1.876	1.874(4)	1.884(2)	1.866(17)	1.853(2)
C═C	1.357	1.350(5)	1.349(4)	1.358(20)	1.38(3)
C−CN	1.422	1.439(6)	1.433(3)	1.439(24)	1.43(3)
C−N	not reported	1.136(5)	1.146(3)	1.138(20)	1.116(3)
			Bond Angles		
Se−M−Se	92.8	93.17(2)	92.08(2)	87.81(7)	91.44(13)
M−Se−C	102.1	101.34(12)	102.86(6)	96.71(48)	97.54(8)
Se−C═C	121.4	121.89(31)	118.18(14)	128.28(1.22)	128.05(1.85)
C═C−CN	121.4	121.33(38)	120.64(11)	117.59(1.48)	114.11(2.22)
C−C−N	178.3	178.87(51)	178.20(23)	177.08(1.90)	175.92(3.15)

[a] $[Ni(mns)_2]^{2-}$; ref 9. [b] $[Ni(mns)_2]^{2-}$ and Ni(dppp)(mns); this work. [c] $[Sb(mns)_2]^{3-}$ and $[Ag(mns)(Se_6)]^{3-}$; ref 10.

In the reaction to form mns, the most likely CN source is acetonitrile. In our original report[10] of the synthesis of $[K([2.2.2]\text{-cryptand})]_3[Sb(mns)_2]$ and $[K([2.2.2]\text{-cryptand})]_3[Ag(mns)(Se_6)]$ (**1**), we proposed that K or $[Ir(cod)Cl]_2$ reacts with ammonia to produce a strong base—KNH_2 or an Ir species,[13,14] respectively. The base likely deprotonates acetonitrile to form a $^-CH_2CN$ species, since $[As(Se)_3(CH_2CN)]^{3-}$ is formed under similar reaction conditions.[10] This proposal is supported here, since the formation of complex **1** has been achieved in the absence of an Ir source and liquid ammonia by introducing the strong base KNH_2 into an acetonitrile solution. The present results provide no insight into what transpires after the proposed deprotonation of acetonitrile. The $^-CH_2CN$ species may couple head to head and be further deprotonated. The $^-CH_2CN$ may react with Se to form an unstable and reactive selenoaldehyde.[15,16] Alterna-

---

(12) Fourmigué, M.; Domercq, B. *Actual. Chim.* **1998**, *11−12*, 9−13.

(13) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 973−976.

(14) Koelliker, R.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 707−709.

(15) Meinke, P. T.; Krafft, G. A. *Tetrahedron Lett.* **1987**, *28*, 5121−5124.

tively, $^{-}CH_2CN$ may react with Se to afford a species that dimerizes in solution to form the mns ligand, similar to the reaction by which the sodium salt of the mnt ligand is formed.[1,17]

Although complex **1** is not the ideal synthon, its reaction with metal chlorides and their derivatives is a viable route to other metal−mns complexes, as illustrated here. For example, the reaction of **1** with a Pd source affords the $Pd(mns)(Se_4)^{2-}$ anion.[18] With the use of such a facile reaction, a variety of new metal−mns complexes may be synthesized and their physical properties systematically studied.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE-9819385). The Quattro II spectrometer was provided by the National Institutes of Health, Grant S10 RR11320.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[K([2.2.2]\text{-cryptand})]_2[Ni(Se_2C_2(CN)_2)_2]$ (**2**) and $Ni(dppp)(Se_2C_2(CN)_2)$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC9901719

---

(16) Kirby, G. W.; Trethewey, A. N. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1913−1922.

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

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

Additions and Corrections

2000, Volume 39

Zenghe Liu and Fred C. Anson*: Electrochemical Properties of Vanadium(III,IV,V)−Salen Complexes in Acetonitrile. Four-Electron Reduction of O_2 by V(III)−Salen.

Page 280. A paragraph describing the available Supporting Information was omitted. The paragraph is provided below.

Supporting Information Available: Three figures showing ^{51}V NMR, ESR, and UV−vis spectra of various vanadium−salen complexes and kinetic plots for the reaction of O_2 with $V^{III}(salen)^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC992000+

10.1021/ic992000+

Published on Web 03/06/2000