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Roles of Bridging Ligand π-Acidity in Determining the Nature of the Lowest Excited States of Binuclear Complexes of Nickel(0). Ligand-Centered ($M_2 \rightarrow \mu$-LCT), Metal-Centered (μ-L $\rightarrow M_2$CT), and Intraligand (IL) Lowest Excited States for the Series of Complexes $Ni_2(\mu\text{-L})(CNMe)_2(PPh_2CH_2PPh_2)_2$ (L = CNR, $CNMe(R)^+$, NO^+)

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The spectroscopy and photochemistry of the series of binuclear Ni(0) complexes $Ni_2(\mu\text{-L})(CNMe)_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane) with either bridging isocyanide ligands (L = CNMe (**1**), CNC_6H_5 (**2**), CN-*p*-C_6H_4Cl (**3**), CN-*p*-C_6H_4Me (**4**)), bridging aminocarbyne ligands (L = $CNMe(C_5H_{11})^+$ (**5**), $CNMe_2^+$ (**6**), $CNMe(CH_2Ph)^+$ (**7**), $CNMe(H)^+$ (**8**), $CNMe(Ph)^+$ (**9**)), or bridging NO^+ (**10**), have been examined. Bridging-ligand substituent effects and solvent dependence of the lowest energy electronic absorption bands of the isocyanide complexes, **1**–**4**, have been interpreted in terms of dimetal to bridging ligand charge transfer ($M_2 \rightarrow \mu$-LCT). This assignment is supported by results of extended Hückel calculations, which indicate a LUMO of predominantly μ-isocyanide π^* character. Bridging-ligand substituent effects on the lowest energy electronic absorption spectral bands of the related aminocarbyne complexes, **5**–**9**, indicate that the direction of charge transfer is reversed compared to the case of the isocyanide complexes. The lowest excited states of the aminocarbyne complexes, **5**–**9**, are assigned to bridging ligand to dimetal charge transfer (μ-L $\rightarrow M_2$CT). This assignment is supported by extended Hückel calculations, which indicate a LUMO of predominantly Ni–Ni antibonding character for the aminocarbyne complexes. The μ-nitrosyl complex $[Ni_2(\mu\text{-NO})(CNMe)_2(dppm)_2][PF_6]$ (**10**) has also been studied. The molecule possesses a structure similar to **1** and **8**. Photochemical reactivity as well as extended Hückel calculations indicates an intraligand (IL) lowest excited state for **10**. Only the $M_2 \rightarrow \mu$-LCT excited state of the μ-isocyanide complexes was found to participate in bimolecular photochemistry. Photolysis of **1** in the presence of CO_2 (1 atm) leads to the [2 + 2] photocycloaddition of CO_2 to the μ-CNMe ligand of **1** and the complex $Ni_2(\mu\text{-CN(Me)C(O)O})(CNMe)_2(dppm)_2$ (**11**). The degree of metal–metal interaction in complexes **1**, **8**, and **10** was found to be related to the Lewis acidity of the bridging ligand. Extended Hückel calculations indicate that the decreasing π^* energies for the series of bridging ligands CNMe, $CN(H)Me^+$, and NO^+ decrease the ground-state contribution of a metal–metal $d\pi^*$ orbital, resulting in increased Ni–Ni interactions. The relative μ-L π^* and Ni–Ni $d\pi^*$ energies also control the nature of lowest excited states as $M_2 \rightarrow \mu$-LCT, μ-L $\rightarrow M_2$CT, and IL for μ-L = CNR, $CNMe(R)^+$, and NO^+, respectively.

Introduction

The photochemistry of binuclear transition-metal complexes remains an area of intense interest.[2] Most organometallic photochemistry of binuclear complexes can be understood to arise via primary photoprocesses that involve either metal–metal bond homolysis, disproportionation, or ligand dissociation. There have been few reports of *associative* organometallic photochemistry.[3-5] We recently reported the first direct evidence for bridging-ligand-centered photochemistry of a binuclear transition-metal complex.[5] The synthesis, structure, chemistry, and photochemistry of the binuclear nickel(0) "cradle" complex $Ni_2(\mu\text{-CNMe})(CNMe)_2(dppm)_2$ (**1**) (dppm = bis(diphenylphosphino)methane) have been described.[5-8] An important aspect of the chemistry of **1** is the N-centered nucleophilicity and basicity of the μ-CNMe ligand. Complex **1** undergoes facile N-protonation, alkylation, and Lewis acid complexation.[6] A reactive triplet $M_2 \rightarrow \mu$-LCT excited state of **1** also undergoes a [2 + 2] cycloaddition reaction with CO_2.[5] In view of the unusual associative photochemistry of **1**, we have examined the electronic spectroscopy of **1** and related μ-isocyanide and μ-aminocarbyne complexes, $Ni_2(\mu\text{-L})(CNMe)_2(dppm)_2$ (L = CNC_6H_5 (**2**), CN-*p*-C_6H_4Cl (**3**), CN-*p*-C_6H_4Me (**4**), $CNMe(C_5H_{11})^+$ (**5**), $CNMe_2^+$ (**6**), $CNMe(CH_2Ph)^+$ (**7**), $CNMe(H)^+$ (**8**), $CNMe(Ph)^+$ (**9**)), as well as the new μ-NO complex $[Ni_2(\mu\text{-NO})(CNMe)_2(dppm)_2][PF_6]$ (**10**). The three types of complexes, μ-isocyanide, μ-aminocarbyne, and μ-nitrosyl, exhibit remarkable differences in the nature of their lowest excited states and photochemistry. Results of ligand substituent effects and solvent dependence of the electronic absorption spectra are presented. These studies indicate the μ-isocyanide complexes **1**–**4** are characterized by lowest excited states that are dimetal to bridging ligand charge transfer ($M_2 \rightarrow \mu$-LCT). The lowest excited states of the μ-aminocarbyne complexes **5**–**9** are found to be bridging ligand to dimetal charge transfer (μ-L $\rightarrow M_2$CT). The μ-nitrosyl complex on the other hand exhibits an intraligand (IL) excited state. Extended Hückel calculations suggest that the electronic structures of complexes **1**–**10** are strongly influenced by the interaction between the Ni–Ni $d\pi^*$ orbitals and the μ-L π^* orbitals. The chemistry, photochemistry, and UV–visible spectra of complexes **1**–**10** are described in terms of their subtle, but important, differences in their electronic structures.

Experimental Section

Materials and Physical Measurements. All manipulations were performed in an N_2 atmosphere by using Schlenk techniques or an inert-atmosphere box. Solvents were reagent grade and were distilled over the appropriate drying agents. Methyl isocyanide and aryl isocyanides were prepared by literature methods.[9] Bromo- and chlorobenzene were purchased from Aldrich Chemical Co. Benzyl iodide was purchased from Alfa, hydriodic acid, 57% solution, from J. T. Baker, and 1-iodo-3-methylbutane from Fluka. ^{1}H NMR and ^{31}P NMR spectra were recorded on a Varian XL-200 or GE-300 spectrometer.[5] The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. Electronic spectra were recorded on an IBM 9420 UV/visible spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer. Microanalyses were performed at Galbraith Laboratories by using a LECO high-temperature analyzer.

Preparation of $Ni_2(\mu\text{-CNMe})(CNMe)_2(dppm)_2$ (1). Complex **1** was prepared as described previously.[6,7]

Preparation of $Ni_2(\mu\text{-CNC}_6H_5)(CNMe)_2(dppm)_2$ (2). Phenyl isocyanide (13 μL, 0.13 mmol) was added to a benzene solution containing complex **1** (0.1246 g, 0.12 mmol). Methyl isocyanide was liberated as

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observed by IR spectroscopy, and the solution color darkened. Benzene was removed by evaporation under vacuum. The remaining residue was redissolved in a minimal amount of benzene, and crystallization was effected by addition of an equal volume of hexane. The red crystalline solid was filtered out, rinsed with acetonitrile and ether, and dried under vacuum; yield 0.115 g, 87%. IR (KBr): ν(CN) 2093 (s), 1995 (m), 1668 (m) cm^{-1}. ^1H NMR: δ 7.81–6.88 (m, 45 H, $(C_6H_5)_2P$, C_6H_5), 3.60 (m, 2 H, PCH_2P), 2.97 (m, 2 H, PCH_2P), 2.09 (s, 6 H, $CNCH_3$). $^{31}P\{^1H\}$ NMR: δ +19.24 (s). UV/vis (benzene): $\lambda_{max} = 395$ nm, $\epsilon = 2.8 \times 10^4$.

$Ni_2(\mu\text{-CN-}p\text{-}C_6H_4Cl)(CNMe)_2(dppm)_2$ (3). Complex **3** was prepared by the method described for complex **2**. IR (benzene): ν(CN) 2094 (s), 1684 (m) cm^{-1}. ^1H NMR: δ 7.81–6.85 (m, 44 H, $(C_6H_5)_2P$, C_6H_4Cl), 3.56 (m, 2 H, PCH_2P), 2.95 (m, 2 H, PCH_2P), 2.09 (s, 6 H, $CNCH_3$). $^{31}P\{^1H\}$ NMR: δ +18.82. UV/vis (benzene): $\lambda_{max} = 395$ nm, $\epsilon = 1.07 \times 10^4$.

$Ni_2(\mu\text{-CN-}p\text{-}C_6H_4Me)(CNMe)_2(dppm)_2$ (4). Complex **4** was prepared as previously described for the preparation of **2**. IR (KBr): ν(CN) 2089 (s), 1667 (m) cm^{-1}. ^1H NMR: δ 7.80–6.85 (m, 45 H $(C_6H_5)_2P$, C_6H_5Me), 3.60 (m, 2 H, PCH_2P), 2.97 (m, 2 H, PCH_2P), 2.21 (s, 3 H, CH_3Ph), 2.10 (s, 6 H, $CNCH_3$). $^{31}P\{^1H\}$ NMR: δ +18.58. UV/vis (benzene): $\lambda_{max} = 395$ nm, $\epsilon = 2.06 \times 10^4$.

$[Ni_2(\mu\text{-CNMe}(i\text{-}C_5H_{11}))(CNMe)_2(dppm)_2]I$ (5). The complex was prepared according to the previously reported procedure for the corresponding methyl complex, **6**.[6] To a solution of **1** (0.1 g) in 20 mL THF was added 1 equiv of $i\text{-}C_5H_{11}I$ (12.9 μL). Precipitation of a dark green crystalline solid was initiated by addition of ~10 mL of hexane. The solid was washed with hexane and dried under vacuum. IR (KBr): ν(CN) 2123 (s), 1516 (m) cm^{-1}. ^1H NMR: δ 7.80–6.90 (m, 40 H, $(C_6H_5)_2P$), 4.29 (m, 2 H, NCH_2–), 3.91 (s, 3 H, $CN(CH_3)\text{-}i\text{-}C_5H_{11}$), 3.43 (m, 2 H, PCH_2P), 3.14 (s, 6 H, $CNCH_3$), 2.94 (m, 2 H, PCH_2P), 2.07 (m, 2 H, $CH_2CH_2CH(Me)_2$), 1.88 (septet, 1 H, $(CH_3)_2CH$), 1.17 (d, 6 H, $(CH_3)_2CH$). $^{31}P\{^1H\}$ NMR: δ +19.92. UV/vis (THF): $\lambda_{max} = 618$ nm, $\epsilon = 5.8 \times 10^2$.

$[Ni_2(\mu\text{-CNMe}_2)(CNMe)_2(dppm)_2]I$ (6). The complex was prepared by literature methods.[6] IR (KBr): ν(CN) 2127 (s), 1512 (m) cm^{-1}. ^1H NMR: δ 7.40–6.85 (m, 40 H, $(C_6H_5)_2P$), 3.93 (s, 6 H, $CN(CH_3)_2$), 3.50 (AA′BB′, 4 H, PCH_2P), 3.21 (S, $CNCH_3$). $^{31}P\{^1H\}$ NMR: δ +20.32 (s). UV/vis (THF): $\lambda_{max} = 620$ nm, $\epsilon = 6.0 \times 10^2$.

$[Ni_2(\mu\text{-CNMe}(CH_2C_6H_5))(CNMe)_2(dppm)_2]Cl$ (7). The complex was prepared from benzyl chloride in a manner similar to the preparation of **6**. IR (KBr): ν(CN) 2129 (s), 1540 (m) cm^{-1}. ^1H NMR: δ 7.55–6.65 (m, 45 H, $(C_6H_5)_2P$, $C_6H_4CH_2$), 3.70 (s, 3 H, $CNCH_3(CH_2Ph)$), 3.29 (m, 2 H, PCH_2P), 2.99 (m, 3 H, $CNCH_3$), 2.74 (m, 2 H, PCH_2P), 2.43 (m, 3 H, $CNCH_3$). $^{31}P\{^1H\}$ NMR: δ +20.72 (AA′BB′). UV/vis (THF): $\lambda_{max} = 585$ nm, $\epsilon = 6.1 \times 10^2$.

$[Ni_2(\mu\text{-CNMe(H)})(CNMe)_2(dppm)_2][X]$ (8) ($X = PF_6$, I). Complex **8** was prepared as the PF_6^- salt by literature methods[6] or by addition of 1 equiv of hydriodic acid to a THF solution of **1**. IR (Nujol): ν(CN) 2135 (s), 1525 (m) cm^{-1}; ν(NH) 3778 cm^{-1}; ν(ND) 2480 cm^{-1} when $F_3C_2O_2D$ was used. ^1H NMR: δ 7.60–6.80 (m, 40 H, $(C_6H_5)_2P$), 3.70 (m, 4 H, PCH_2P), 3.28 (s, 6 H, $CNCH_3$), 2.48 (s, 3 H, $CN(H)CH_3$). $^{31}P\{^1H\}$ NMR: δ 19.75 (AA′BB′).

$[Ni_2(\mu\text{-CNMe(Ph)})(CNMe)_2(dppm)_2][X]$ (9) (X = Cl, Br, I). Complex **9** can be prepared by photolysis, $\lambda_{exc} = 366$ nm, of a chloro- or bromobenzene solution of **1** or, as the iodide, by addition of excess iodomethane (3.0 mL, 0.05 mmol) to a THF solution of **2** (0.026 g, 0.025 mmol). The complex slowly crystallizes from solution. Further precipitation was effected by addition of hexane. The crystalline solid was filtered out, rinsed with hexane, and dried under vacuum; yield 0.027 g, 92%. IR (KBr): ν(CN) 2137 (s), 1523 (m) cm^{-1}. ^1H NMR: δ 7.72–6.90 (m, 45 H, $(C_6H_5)_2P$, C_6H_5), 4.28 (s, 3 H, $CN(CH_3)Ph$), 3.53 (m, 2 H, PCH_2P), 3.00–2.83 (overlapped, 8 H, $CNCH_3$, PCH_2P). $^{31}P\{^1H\}$ NMR: δ +20.2 (AA′BB′). UV/vis (THF): $\lambda_{max} = 550$ nm, $\epsilon = 1.6 \times 10^3$. The photochemical reactions of **1** with chloro- or bromobenzene were monitored by infrared spectroscopy, following the disappearance of **1** (ν(CN) 2075, 1717 cm^{-1}) in neat C_6H_5X (X = Br, Cl). Electronic absorption spectroscopy was also used to monitor the decrease in absorption at 395 nm and increase at 550 nm. The quantum yield for disappearance of **1** in C_6H_5Cl or C_6H_5Br was determined to be $\Phi_{366} = 0.05 \pm 0.01$ in both cases.

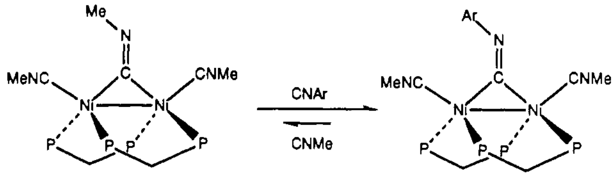
$[Ni_2(\mu\text{-NO})(CNMe)_2(dppm)_2][PF_6]$ (10). Nitrosyl hexafluorophosphate (0.050 g, 0.27 mmol) was added to a toluene solution containing complex **1** (0.300 g, 0.30 mmol) that was cooled to 0 °C. After 1 h the solution had darkened. The solution was warmed to 25 °C and stirred for 12 h. The green solid was collected by filtration, washed with toluene and hexanes, and then dried under vacuum; yield 0.260 g, 84% based on $NOPF_6$. IR (KBr): ν(CN) 2170 (s) cm^{-1}; ν(NO) 1536 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR: δ 24.88 (s). ^1H NMR: δ 7.30 (m, 40 H, $(C_6H_5)_2P$), 3.45 (m, 2 H, PCH_2P), 3.32 (s, 6 H, $CNCH_3$), 2.90 (m, 2 H, PCH_2P). UV/vis (λ_{max}, nm (ϵ)): 267 (24 800), 328 (16 650), 433 (3930), 669 (1430), 756 (1150). The crystal and molecular structure of **10** is described elsewhere.[10]

$Ni_2(\mu\text{-CNC(O)O(Me)})(CNMe)_2(dppm)_2$ (11). Complex **11** was prepared as previously described[7] or by photolysis, $\lambda_{exc} = 366$ nm, of a THF solution of **1** under an atmosphere of CO_2, $\Phi_{366} = 0.05$. IR (KBr): ν(CN) 2134 (s), 1528 (m); ν(CO) 1727 (m, br), 1464 (m) cm$^-$11. $^{31}P\{^1H\}$ NMR: δ 22.4 (AA′BB′). The photochemical reaction of **1** with CO_2 was monitored by infrared spectroscopy by following the decrease in ν(CN) at 2075 and 1717 cm^{-1} and the appearance of a characteristic ν(CN) band of **11** at 2134 cm^{-1}.

Molecular Orbital Calculations for $Ni_2(\mu\text{-CNR})(CNR)_2(PH_2CH_2PH_2)_2$, $[Ni_2(\mu\text{-(CNRR')}(CNR)_2(PH_2CH_2PH_2)_2]^+$, and $[Ni_2(\mu\text{-NO})(CNR)_2(PH_2CH_2PH_2)_2]^+$. Calculations were performed for $Ni_2(\mu\text{-CNH})(CNH)_2(PH_2CH_2PH_2)_2$, $[Ni_2(\mu\text{-CNH}_2)((CNH)_2(PH_2CH_2PH_2)_2]^+$, and $[Ni_2(\mu\text{-NO})(CNH)_2(PH_2CH_2PH_2)_2]^+$ by using the extended Hückel method.[11] The parameters used for nickel were developed earlier by Hoffmann[12] and adapted in the present study. The experimentally determined Ni–Ni bond lengths of 2.572 (1) Å for **1**,[6] 2.500 (1) Å for **8**,[6] and 2.471 (2) Å for **10**[10] were used. The remainder of the geometrical parameters were averages of experimental findings with modifications to conform to C_s symmetry.

Results and Discussion

Preparation of the μ-Aryl Isocyanide Complexes, 2–4, by μ-CNMe Substitution of 1. Substitution reactions of the tris(methyl isocyanide) complex **1** show that, upon substitution of one CNMe by another ligand, the strongest π-acceptor binds to the dinickel core in the bridging position. The aryl isocyanides CNAr (Ar = C_6H_5, C_6H_4Cl, C_6H_4Me) are recognized as stronger π-acceptors than CNMe; and thus upon addition of 1 equiv of CNAr, the μ-CNMe ligand is replaced (eq 1). A partial vacuum placed over the system facilitates the removal of volatile methyl isocyanide. The red-orange complexes were prepared in high yield and recrystallized from benzene/hexane. The symmetric μ-CNAr structures of the resulting $Ni_2(\mu\text{-CNAr})(CNMe)_2(dppm)_2$ complexes (Ar = C_6H_5 (**2**), C_6H_4Cl (**3**), C_6H_4Me (**4**)) are evident by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectra of each complex show two equivalent MeNC ligands; and the $^{31}P\{^1H\}$ NMR spectra are simple singlets to −40 °C. These data indicate average symmetric structures, suggesting equilibration between bending μ-CNAr conformers, but clearly indicate that the CNAr ligands are uniquely bridging. The IR spectra of **2–4** display ν(CN) values in the range 1667–1684 cm^{-1} for the stronger π-acceptor μ-CNAr ligands, compared to 1717 cm^{-1} for **1**. Similarly, the terminal CNMe ν(CN) values of **2–4** occur approximately 10 cm^{-1} higher in energy than those of **1**.



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(1)

Preparation of the Aminocarbyne Complexes $[Ni_2(\mu\text{-CNRR'})(CNMe)_2(dppm)_2][X]$ (5–9) by N-Alkylation and N-Arylation. Complex **1** exhibits significant reactivity associated with the μ-CNMe nitrogen atom.[5-7] The nitrogen atom of the bridging methyl isocyanide possesses a Lewis basicity stronger than that of ammonia.[6] A variety of weak acids such as AcOH, PyH^+, and PhOH protonate the μ-CNMe nitrogen atom to form the aminocarbyne complex **8**.[6] Similarly, the alkyl halides RX ($i\text{-}C_5H_{11}I$, MeI, $C_6H_5CH_2Cl$) react with **1** to form the N-alkylated aminocarbyne complexes **5–7** (eq 2). The corresponding arylated aminocarbynes $[Ni_2(\mu\text{-CNMe(Ph)})(CNMe)_2(dppm)_2][X]$ (**9**) (X = Cl, Br, I) were prepared by the photochemical N-arylation of **1** with phenyl chloride or phenyl bromide,[5] or alternatively by the reaction of the μ-CNPh complex, **2**, with MeI. Complexes **5–9**

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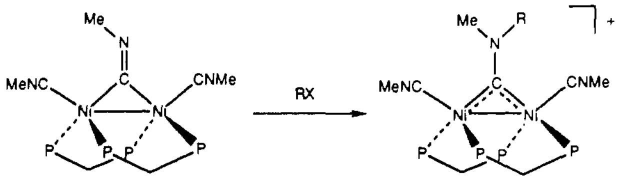

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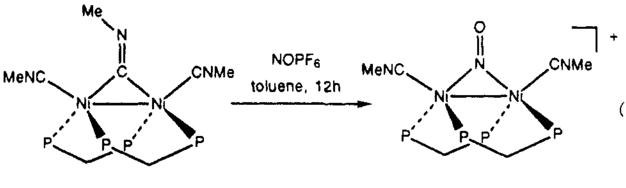
(2)

were all isolated as emerald green solids and were recrystallized from THF/hexane. Complex **8** was characterized previously by X-ray diffraction.[6] All other aminocarbyne complexes were characterized by spectroscopic methods. The (dimethylamino)carbyne complex, **6**, displays a singlet $^{31}P\{^1H\}$ NMR signal. The remaining asymmetrically substituted aminocarbyne complexes, **5** and **7–9**, display characteristic AA′BB′ signals. In the IR spectra of **5–9**, the aminocarbyne ν(CN) bands occur at very low energies over the range 1512–1525 cm^{-1}.

Preparation of $[Ni_2(\mu\text{-}NO)(CNMe)_2(dppm)_2][PF_6]$ (10). The preparation of the μ-nitrosyl complex $[Ni_2(\mu\text{-}NO)(CNMe)_2(dppm)_2][PF_6]$ (**10**) was accomplished by the substitution of the bridging methyl isocyanide in $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ (**1**) with the NO^+ ligand. Complex **1** was dissolved in toluene, and an equimolar quantity of $NOPF_6$ was added. After 12 h, the orange solution containing the tris(isocyanide) complex gave way to a green precipitate, $[Ni_2(\mu\text{-}NO)(CNMe)_2(dppm)_2][PF_6]$ (**10**), in ≈90% yield (eq 3). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 24.88 ppm, similar to other symmetric dinuclear nickel(0) cradle complexes. The ^1H spectrum shows a singlet at 3.32 ppm due to two equivalent terminal methyl isocyanides. The ^1H NMR spectrum of **10** also indicates the presence of two methylene proton environments of the dppm. The methylene signals at 3.45 and 2.90 ppm are assigned to the endo and exo methylene protons. Significantly, this indicates that, in contrast to other "cradle" complexes, a rigid cis,cis "cradle" structure is retained in solution.[6] The infrared spectrum shows a terminal isocyanide stretch at 2170 cm^{-1} and an intense band at 1536 cm^{-1}, which has been assigned to the bridging nitrosyl group. The low value of ν(NO) indicates that there is substantial back-bonding into the π^* orbitals of the nitrosyl group.



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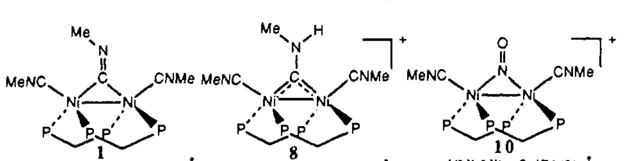
10

(3)

The structure of **10** was determined by X-ray diffraction.[10] The structure consists of two approximately tetrahedrally coordinated Ni(0) centers with *cis*, *cis*-diphosphines. The overall structure is that of a binuclear "cradle" type complex[6,7] and is very similar to the structures of **1** and **8**. The Ni–Ni bond length of 2.471 (2) Å is well within the range for Ni–Ni single bonds[13–19] and significantly shorter than the corresponding distances found in **1** and **8**. It is interesting to note that for a d^{10}–d^{10} binuclear complex no d-orbital-based M–M bonding is feasible because the entire d manifold is filled. In the case of strongly π-accepting bridging ligands, however, $d\pi^*$ electron density may be assigned to the π acceptor, in effect canceling a metal–metal antibonding interaction. The greater the π^*-back-bonding ability, the stronger the M–M bonding interaction is expected to be. This trend is well illustrated by the series of analogous compounds **1**, **8**, and **10**. For the μ-isocyanide (**1**), μ-aminocarbyne (**8**), and μ-nitrosyl (**10**) complexes, which have been structurally characterized, the degree of metal–metal interaction increases as the Lewis acidity of the bridging ligand increases. The nitrosyl ligand is generally regarded to be the strongest π-acceptor diatomic ligand, and the nitrosyl complex **10** possesses a significantly shorter Ni–Ni distance.



1
d(Ni-Ni)= 2.572(1) Å

8
d(Ni-Ni)= 2.500(1) Å

10
d(Ni-Ni)= 2.471(2) Å

Electronic Absorption Spectra of d^{10}–d^{10} Binuclear Complexes. The nature of the lowest energy electronic absorption spectral bands for the isocyanide complexes **1–4** was assessed by bridging ligand substituent and solvent effects. The electronic absorption spectrum of **1** exhibits an intense, broad band centered at λ_{max} = 345 nm (ϵ = 19000 M^{-1} cm^{-1}) in THF solution. The UV/vis spectroscopic data for the isocyanide complexes, **1–4**, appear in Table I. Within the group of μ-aryl isocyanide complexes **2–4**, values of λ_{max} are quite insensitive to the nature of the para substituent on the aryl group but are shifted to longer wavelengths by 35 nm relative to the μ-methyl isocyanide complex **1** in THF. There are also significant intensity differences between the aryl complexes **2–4** and **1**. The values of ϵ determined for the aryl complexes **2–4** are 20–100% higher than the values for **1** in THF and benzene. The intensity increases, resulting from replacement of an alkyl substituent with aryl substituents, have been addressed and are consistent with electronic delocalization onto the aryl substituents.[4] This can be seen further by the decrease in intensity upon placing an electron-donating group at the para position. The effect of the electron-withdrawing halogen in the para position is complicated by its resonance effects and may reflect the halogen's inability to further delocalize electron density onto the aryl ring. The bathochromic shifts and intensity increases resulting from replacement of an alkyl substituent with aryl substituents are consistent with metal to μ-ligand charge transfer ($M_2 \rightarrow \mu$-LCT). The electronic absorption spectra of the μ-isocyanide complexes, **1–4**, also exhibit significant solvent dependence. Hypsochromic shifts as large as 85 nm (THF/MeCN) are observed in more polar solvents. This is consistent with a Franck–Condon destabilized excited-state model in which a polar solvent is unable to reorient itself in response to an excited state of polarity markedly different from that of the ground state. Extended Hückel calculations support the notion of metal to bridging ligand charge transfer (vide infra).

A remarkable reversal of the direction of charge transfer occurs in the N-alkylated and N-arylated aminocarbyne complexes $Ni_2(\mu\text{-}L)(CNMe)_2(dppm)_2$ where L = $CNMe(C_5H_{11})^+$ (**5**), $CNMe_2^+$ (**6**), $CNMe(CH_2Ph)^+$ (**7**), $CNMe(H)^+$ (**8**), and $CNMe(Ph)^+$ (**9**). The UV/visible electronic absorption spectral data for these complexes are found together with the corresponding data for the μ-isocyanide complexes, **1–4**, in Table I. A substituent dependence is observed for the aminocarbyne complexes, **5–9**. In THF, the observed values of λ_{max} depend strongly on the electron-donating character of R. The bridging ligand with the strongest electron-donor substituent, L = $CNMe(C_5H_{11})^+$ (**5**), exhibits the lowest energy optical excitation, λ_{max} = 618 nm. The bridging ligand with the weakest electron-donor substituents, L = $CNMe(Ph)^+$ (**9**), shows a corresponding value of λ_{max} = 550 nm. The increase in the energies of the lowest energy optical transitions with decreased electron-donor ability of the μ-aminocarbyne substituents is clearly consistent with ligand to metal charge transfer. The reversal of the substituent effects in the μ-isocyanide complexes, **1–4**, compared to the μ-aminocarbyne complexes, **5–9**, is best explained by an inversion of the *HOMO* upon alkylation. The effect of an aryl substituent is again in the increased intensity of the electronic transition of 10-fold over the other (alkylamino)carbyne complexes. The observed spectral dependence of the aminocarbyne complexes is best described by

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Table I. UV/Vis Data for $Ni_2(\mu\text{-}L)(CNMe)_2(dppm)_2$ with Different Bridging Ligands, L

	λ_{max} (benzene), nm	ϵ (benzene), $M^{-1}\ cm^{-1}$	λ_{max} (THF), nm	ϵ (THF), $M^{-1}\ cm^{-1}$
CNMe (**1**)	395	1.4×10^4	345	1.9×10^4
CNC_6H_5 (**2**)	395	2.8×10^4	380	3.3×10^4
CN-*p*-C_6H_4Cl (**3**)	395	1.7×10^4	380	2.7×10^4
CN-*p*-$C_6H_4CH_3$ (**4**)	395	2.1×10^4	380	2.3×10^4
$CNMe(i\text{-}C_5H_{11})^+$ (**5**)			618	5.8×10^2
$CNMe_2^+$ (**6**)			620	6.0×10^2
$CNMe(CH_2C_6H_5)^+$ (**7**)			585	6.1×10^2
$CNMe(H)^+$ (**8**)			570	6.1×10^2
$CNMe(C_6H_5)^+$ (**9**)			550	1.6×10^3

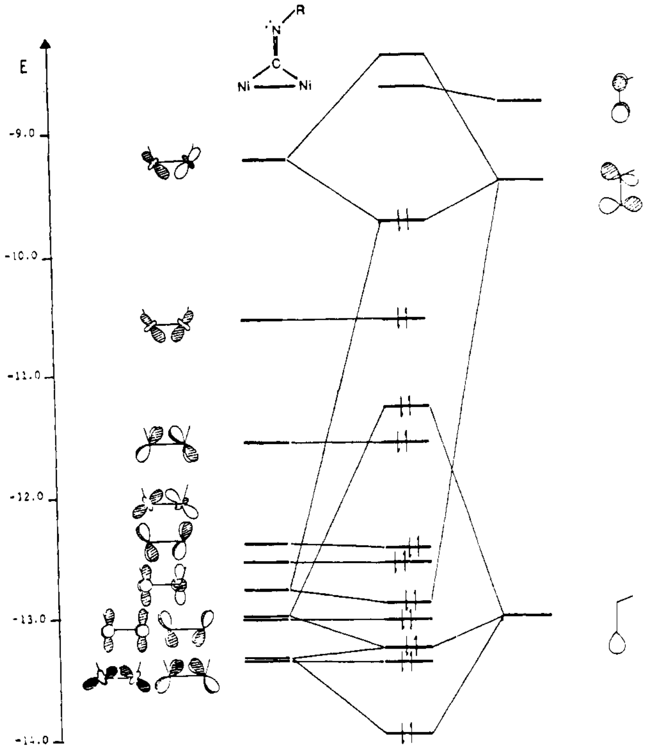

Figure 1. Extended Hückel orbital energy diagram for the interaction of a μ-CNH ligand with a $Ni_2(CNH)_2(PH_2CH_2PH_2)_2$ framework.

a bridging ligand to metal charge-transfer (μ-L → M_2CT) process.

The UV/vis electronic absorption spectrum of the nitrosyl complex **10** exhibits three distinct bands between 300 and 900 nm with extinction coefficients greater than 1500 $M^{-1}\ cm^{-1}$. Unlike those of the isocyanide and aminocarbyne complexes however, the UV/vis spectrum for the nitrosyl complex is essentially solvent independent. The spectroscopic results combined with results of extended Hückel calculations suggest that the nitrosyl complex **10** possesses an excited state characterized by relatively small change in the charge distribution of the complex.

Molecular Orbital Calculations. Extended Hückel calculations[11,12] were undertaken to examine the metal–ligand interactions which control the nature of the HOMO and LUMO in d^{10}–d^{10} binuclear complexes. Our chemical, photochemical, and spectroscopic studies show how exquisitely sensitive the electronic structure of d^{10}–d^{10} binuclear complexes is to the nature of the bridging ligand. Simplified model complexes were used where the phenyl groups of dppm were replaced by H atoms, as were the alkyl groups of the μ-isocyanide and the μ-aminocarbyne. The replacement of these groups by H may affect the individual electronic structures; however the comparison between the members of the series μ-CNH, μ-CNH_2^+, and μ-NO^+ is expected to reveal the trends in electronic structural changes that result from substitution of the bridging ligand. Of particular interest is the character of the HOMO and LUMO as well as the extent of metal–metal interactions in these compounds. Molecular geometries were taken from the crystal structures of **1**,[6] **8**,[6] and **10**.[10] A summary of the orbital interactions and energies for the μ-isocyanide complex is depicted in Figure 1. The results indicate that the HOMO is the result of a Ni_2 dπ* and μ-CNR π* interaction. The HOMO therefore has significant metal character. The LUMO, on the other hand, is found to be essentially purely μ-isocyanide π* in character. We note that the terminal isocyanide π* orbitals lie significantly higher in energy and are not included in the diagram. Figure 2 presents an extended Hückel molecular orbital plot for the HOMO of the μ-isocyanide/Ni_2 interaction. The corresponding LUMO for the μ-isocyanide/Ni_2 interaction is given in Figure 3. The calculation illustrates a significant admixture of dπ* orbitals from the Ni_2 framework with the μ-isocyanide ligand in the ground state. The mixing of dπ* metal orbitals with the ordinarily vacant μ-CNR π* level diminishes the importance of the metal–metal antibonding levels and provides the mechanism for the formation of bonds in a d^{10}–d^{10} system. The essentially purely μ-isocyanide ligand based LUMO is also fully consistent with the existence of a low-lying excited state which would best be described as Ni_2 → μ-CNR π* for the μ-isocyanide complexes.

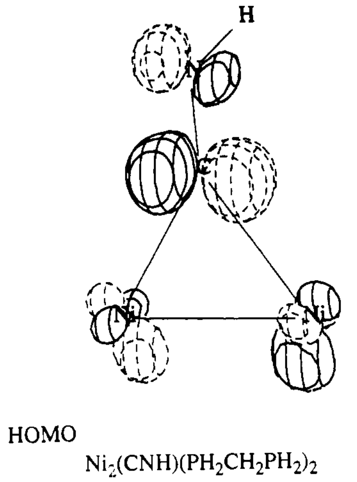

Figure 2. Extended Hückel molecular orbital plot of the HOMO resulting from the interaction of a μ-CNH ligand with a $Ni_2(CNH)_2(PH_2CH_2PH_2)_2$ framework.

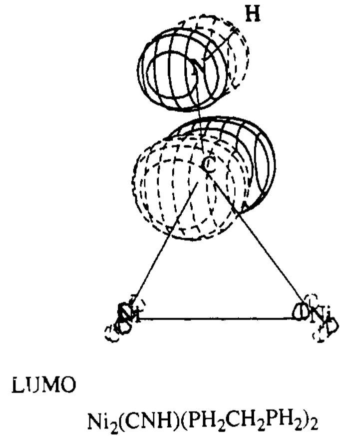

Figure 3. Extended Hückel molecular orbital plot of the LUMO resulting from the interaction of a μ-CNH ligand with a $Ni_2(CNH)_2(PH_2CH_2PH_2)_2$ framework.

The extended Hückel molecular orbital interaction energy diagram for the corresponding μ-aminocarbyne/Ni_2 interaction is presented in Figure 4. There are subtle, but important, differences compared to the case of the isocyanide. The aminocarbyne acceptor p orbital is significantly lower in energy relative to the π* energies of the μ-isocyanide. Consequently, there is a greater admixture of the aminocarbyne p orbital and less Ni_2 dπ* character in the HOMO. This has the effect of strengthening the metal–metal interaction in the ground state of the μ-amino-

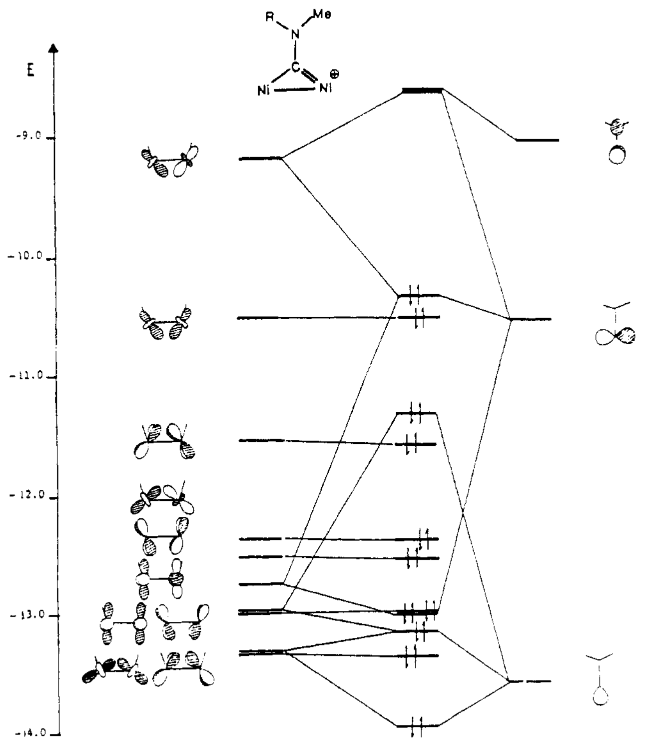

Figure 4. Extended Hückel orbital energy diagram for the interaction of a μ-CNH_2^+ ligand with a $Ni_2(CNH)_2(PH_2CH_2PH_2)_2$ framework.

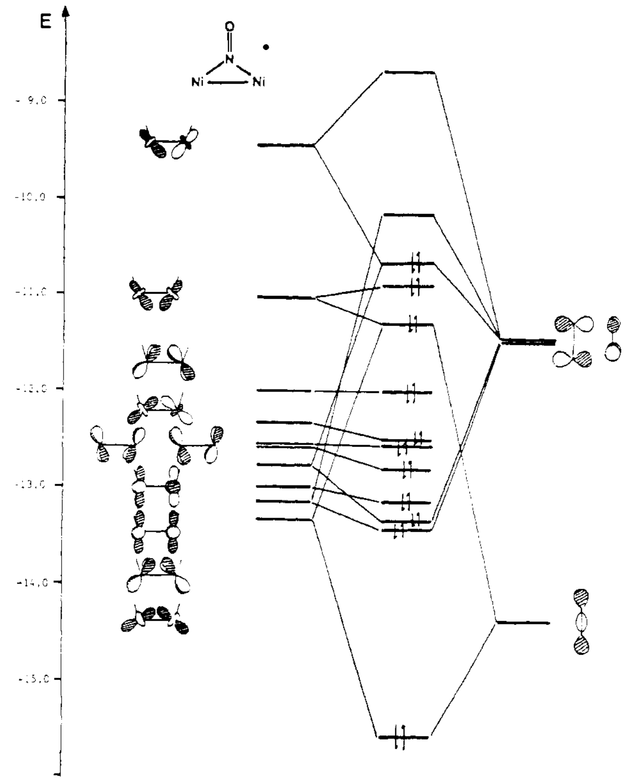

Figure 5. Extended Hückel orbital energy diagram for the interaction of a μ-NO^+ ligand with a $Ni_2(CNH)_2(PH_2CH_2PH_2)_2$ framework.

carbyne compared to the μ-isocyanide. There is also a corresponding increase in Ni_2 dπ* character of the LUMO. The large μ-aminocarbyne ligand contribution to the HOMO and Ni_2 dπ* contribution to the LUMO support the spectroscopic observation of a μ-L → Ni_2 charge-transfer lowest excited state for the aminocarbyne complexes, **5**–**9**.

The extended Hückel orbital energy diagram for the interaction of NO^+ with the Ni_2 core is presented in Figure 5. The nitrosyl represents the extreme for the Ni_2 dπ*/μ-ligand π* interactions found in the d^{10}–d^{10} binuclear cradle frameworks. The two π* orbitals of the nitrosyl are significantly deeper in energy than either the μ-aminocarbyne or the μ-isocyanide π-acceptor orbitals; and they strongly interact with the dπ* orbitals of the nickel atoms. The HOMO is an admixture of the d_{yz} orbitals of the Ni_2 core, the empty π* orbital of NO^+, and a $d_{xy,yz}$ orbital of the metal core. The Ni_2 dπ*/μ-NO^+ π* interaction is the strongest of the series of the three systems examined; and therefore the strongest "anti-antibond" is expected. This is in agreement with the trend in Ni–Ni distances decreasing for the series μ-CNR > μ-$CNRR'^+$ > μ-NO^+ noted above. However, the HOMO and LUMO orbital compositions are extremely similar in the case of the μ-NO^+ system. The essentially equal contributions of Ni_2 dπ* and μ-NO^+ π* orbitals to the HOMO and LUMO of the μ-NO^+ system tend to eliminate the possibility of the large charge redistributions which are predicted from these theoretical studies and supported by experimental findings for the μ-isocyanide and μ-aminocarbyne systems.

Conclusions Regarding Electronic Structure and CO_2 Activation. Our spectroscopic and theoretical studies of the electronic structures of the d^{10}–d^{10} binuclear cradle complexes reveal a surprising complexity. The lowest excited states of the μ-isocyanide complexes, **1**–**4**, are Ni_2 → μ-CNR π* charge transfer. In the case of the μ-aminocarbyne complexes, **5**–**9**, there is a reversal of the direction of charge transfer in the lowest excited state to μ-L → Ni_2. The nitrosyl complex **10** is uniquely unreactive chemically and photochemically. An even balance of μ-NO^+ and Ni_2 contributions to the HOMO and LUMO of the nitrosyl suggests that charge transfer should not figure prominently in its photochemistry. The μ-isocyanide complexes, **1**–**4**, are unique in their ability to photochemically activate CO_2 through their Ni_2 → μ-CNR π* charge-transfer triplet excited state. This model provides an interesting comparison to the well-studied n,π* photochemistry of organic ketones and imines.[20] An important distinction of the Ni_2 → μ-CNR π* excited state is reverse polarization compared to an n,π* excited state of an organic imine.

Ni_2 dπ* →μ-CNRπ• n,π*

Therefore, in contrast to the n,π* photochemistry of organic imines, which undergo dipolar [2 + 2] additions, complexes possessing a Ni_2 → μ-CNR π* excited state should show enhanced reactivity in reactions already associated with the ground state. The μ-methyl isocyanide complex, **1**, reacts thermally with electrophiles, producing bridging aminocarbyne complexes. The nucleophilicity of the μ-isocyanide N atom is expected to be enhanced by photoexcitation. This is consistent with the observation of the formation of the CO_2 cycloadduct Ni_2(μ-CN(Me)C(O)O)$(CNMe)_2(dppm)_2$,[7] from **1** at only 1 atm of CO_2 pressure, while the corresponding thermal reaction requires liquid CO_2 solvent, 1400 psi pressure, and 24-h reaction time. The observation of excited-state reactivity of **1** toward N-arylation by aryl chlorides, however, suggests that there may be significant electron-transfer character to this unusual excited state, similar to an S_{RN1} reaction of an aryl halide. The comparison of charge distributions in the Ni_2 → μ-CNR π* excited state of **1** and the n,π* state of an imine suggests that the regiochemistry of [2 + 2] cycloadditions with asymmetric olefinic substrates should be opposite. To date, we have not been able to test this hypothesis, owing to the lack of stability of most cycloadducts of **1** and related μ-isocyanide cradle complexes.

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Conclusion

A series of d^{10}–d^{10} binuclear cradle complexes with μ-isocyanides (**1**–**4**), μ-aminocarbynes (**5**–**9**), and μ-nitrosyl (**10**) have been prepared and the electronic structures compared. A $Ni_2 \rightarrow \mu$-CNR π^* excited state of complexes **1**–**4** provides the unique ability to activate CO_2 by an *associative* pathway.[5] Due to the stability of the dinickel cradle core, a systematic study of the effects of placing different π-acceptor ligands in the bridgehead position was possible. The degree of π-acceptor ability of the bridging ligand results in profound changes in the degree of metal–metal bonding and the frontier orbitals. The series of μ-isocyanide, μ-aminocarbyne, and μ-nitrosyl compounds have also demonstrated a remarkable difference in their photochemistry, owing to their subtle differences in electronic structure. The bridging isocyanide complexes show low-lying excited states that are described as MLCT; the aminocarbyne complexes show excited states that are described as LMCT; and the nitrosyl complex is best described as having an IL lowest energy excited state.

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Complexes of the Ligand 1,5,8,12-Tetraazadodecane (3,2,3-tet) with Manganese(III) and with a Valence-Trapped Manganese(III)/Manganese(IV) Hexanuclear Array. Crystal and Molecular Structures of [*trans*-Mn(3-IOBz)$_2$(3,2,3-tet)](ClO_4) and [Mn_6(3,2,3-tet)$_4O_6$(OAc)$_3$]I_5·$2H_2O$·$4C_4H_8O$

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Mononuclear Mn(III) complexes containing two coordinated carboxylates and the tetraamine 1,5,8,12-tetraazadodecane (3,2,3-tet) have been synthesized by using substituted benzoates. The complexes *trans*-bis(3-iodobenzoato)(1,5,8,12-tetraazadodecane)-manganese(III) perchlorate (**6**) and *trans*-bis(4-nitrobenzoato)(1,5,8,12-tetraazadodecane)manganese(III) iodide (**7**) were prepared, and **6** was structurally characterized. Complex **6** crystallizes in the monoclinic space group $P2_1/c$, $Z = 4$, with $a = 22.973$ (9) Å, $b = 12.029$ (3) Å, $c = 10.833$ (5) Å, and $\beta = 102.38$ (3)°, and the structure has been refined to an R of 0.035. The geometry around the Mn(III) ion is an irregular octahedron with monodentate benzoato ligands bound in trans positions. With acetate and benzoate as the carboxylate groups, a number of hexanuclear species have been isolated. A hexanuclear complex [Mn_6-(3,2,3-tet)$_4$(OAc)$_3O_6$]I_5·$2H_2O$·$4C_4H_8O$ (**3**) has been structurally characterized. It crystallizes in the monoclinic space group $C2/c$, $Z = 4$, with $a = 27.733$ (13) Å, $b = 13.663$ (7) Å, $c = 27.020$ (14) Å, and $\beta = 124.16$ (3)°, and the structure has been refined to an R of 0.055. The asymmetric unit contains three types of manganese ions, a Mn(IV) ion octahedrally coordinated to a 3,2,3-tet ligand and two μ_2-oxo groups, a Mn(III) ion coordinated to a 3,2,3-tet ligand, a μ_3-oxo group, and a μ_2-acetato ligand, and a Mn(III) ion with six oxygen donor atoms, two μ_2-oxo groups, two μ_3-oxo groups, and two μ_2-acetato groups. Preparation of related benzoate complexes is also described. ESR, infrared, and visible spectra of these complexes have been measured and are discussed.

Introduction

The chemistry of manganese in oxidation states III–V is relatively sparse but is under active investigation. Most of the complexes that have been characterized over the last few years are polynuclear with μ-oxo and/or μ-carboxylato groups linking two,[1–16] three,[14g,17–19] or four[14a,20–25] manganese ions. However, species with six,[25,26] seven,[27] nine,[28] ten,[29] and twelve[30] manganese ions have also been reported. The discovery of these complexes suggests that Mn(III) and Mn(IV) have a rich and complex chemistry which is of considerable interest in developing models for the oxygen-evolving complex in photosynthesis,[31,32] manganese-containing catalases,[33,34] ribonucleotide reductases,[35] and superoxide dismutases.[36] The chemistry and biochemistry of these systems has been the subject of a number of recent reviews.[37]

Mononuclear complexes of Mn in the III and IV oxidation states have received much less attention recently, but such complexes are known with amine, phosphine, and arsine oxide ligands,[38] macrocyclic triamines,[39] tetraamines,[40,41] and pentaamines,[42] amino carboxylates,[43] catecholates,[44] a variety of Schiff base ligands,[45–48] and porphyrins.[49] A recent report has described a mononuclear Mn(V) complex.[50]

We have prepared and are attempting to characterize mixed-ligand complexes of Mn(III) and Mn(IV) with linear polyamines, such as diethylenetriamine (1,4,7-triazaheptane), triethylenetetramine (1,4,7,10-tetraazadecane), 2,3,2-tet (1,4,8,11-tetraazaundecane), and 3,2,3-tet (1,5,8,12-tetraazadodecane), and carboxylate anions, such as acetate and benzoate.[19,27] In most

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