ly.[12,13,15,16,43,44] In our view the very small Cr(1)–O(1)–Cr(2) bridging angle of 142.8 (5)° as compared with 154–166° reported for the rhodo salts is partially responsible for this difference. A discussion of such relations will be the subject of future publications from our laboratories.

Acknowledgment. We are very grateful to Mrs. Solveig Kallesøe, who performed most of the susceptibility measurements, and to Ms. Suzanne Byrd and Ms. Shaina Virji for assistance in the collection and reduction of the crystallographic data. This work was supported by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO), through Grant 1318 and by the Danish National Science Research Council through Grant 511-3993.

Registry No. $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$, 15007-47-3; *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)](S_2O_6)_2\cdot 3H_2O$, 74410-09-6; *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]Cl_4$, 74365-64-3.

Supplementary Material Available: A table of anisotropic thermal parameters and a list of observed and calculated structure amplitudes (electrons × 10) (10 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Bis(δ-camphorquinone dioximato)nickel(II) and -palladium(II). Reactions and Structural Studies of Some M_3Ag_3 Cluster Complexes of Camphorquinone Dioxime

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Reactions of $AgNO_3$ with Ni(δ-HCQD)$_2$ or Pd(δ-HCQD)$_2$, where δ-HCQD$^-$ is δ-camphorquinone dioximato, yielded the hexanuclear metal cluster complexes [Ni(δ-HCQD)$_2$Ag]$_3$·2.5CHCl$_3$, Ni–Ag, and [Pd(δ-HCQD)$_2$Ag]$_3$·2CHCl$_3$, Pd–Ag, respectively. X-ray crystallographic studies performed on both complexes showed them to belong to space group $P2_12_12_1$. The unit cell dimensions of Ni–Ag are a = 15.990 (5) Å, b = 38.44 (1) Å, c = 13.437 (5) Å, V = 8260.97 Å^3, and Z = 4 while those of Pd–Ag are a = 16.110 (6), b = 38.92 (1), c = 13.393 (3) Å, V = 8395.55 Å^3, and Z = 4. Block-diagonal least-squares refinement of 3021 observed reflections for Ni–Ag and 6112 for Pd–Ag converged to R_F = 10.7 and 11.4 (R_w = 12.7 and 15.0) for the Ni–Ag and Pd–Ag structures, respectively. Their structures indicate that each hexanuclear molecule consists of three individual M(δ-HCQD)$_2^-$ units which act as multidentate ligands coordinating to a linear chain of three silver atoms. The coordination geometry around each M ion in the M(δ-HCQD)$_2^-$ units is square planar, and the δ-HCQD$^-$ ligands are coordinated to M via N and O atoms. The Ag in the center of the molecule is coordinated to six O atoms with average Ag–O distances of 2.49 (3) and 2.45 (2) Å for Ni–Ag and Pd–Ag, respectively. The two silver atoms at the ends of the chain are each coordinated to three nitrogen atoms from the M(δ-HCQD)$_2^-$ units with average Ag–N distances of 2.20 (4) and 2.27 (3) Å, respectively. The Ag–Ag distances, 3.059 (5) and 3.052 (5) Å in Ni–Ag and 3.173 (3) and 3.179 (3) Å in Pd–Ag, are somewhat longer than those (2.89 Å) in Ag metal and indicate that there are Ag–Ag interactions along the linear chains. The bis(pyridine) adduct of Ni(δ-HCQD)$_2$ was also prepared. A proposed structure for this complex is based on the similarity of its IR spectrum to those of the Ni–Ag and Pd–Ag clusters.

Introduction

Our earlier work,[1,2] as well as that of Nakamura et al.,[3] showed that α- and δ-camphorquinone dioximes (H_2CQD) form square-planar Ni(II) and Pd(II) complexes in which the ligands chelate via nitrogen and oxygen donor atoms. The structure[1] of Ni(δ-HCQD)$_2$ is shown in Figure 1.

In the present paper, we report the reactions of Ni(δ-HCQD)$_2$ and Pd(δ-HCQD)$_2$ with $AgNO_3$ to form hexanuclear clusters of the composition [M(δ-HCQD)$_2$Ag]$_3$, where M is Ni(II) or Pd(II). Results of crystallographic studies on both of these complexes are described. It has also been found that Ni(δ-HCQD)$_2$ reacts with pyridine to give an adduct whose proposed structure is related to that of the clusters.

Experimental Section

Spectral Data. Proton NMR spectra were obtained by using a Varian HA-100 spectrometer with Me_4Si as the internal reference and $CDCl_3$ as the solvent. The ^{13}C NMR spectra were recorded on a JEOL FX-90Q ^{13}C NMR/^1H spectrometer. Infrared spectra were obtained on KBr pellets with a Beckman IR-4250 (4000–200 cm^{-1}) spectrophotometer. Electronic spectra were recorded on a JASCO-ORD/UV-5 or Cary 14 spectrophotometer.

Starting Materials. The complexes Pd(δ-HCQD)$_2$, Ni(δ-HCQD)$_2$, and Ni(α-HCQD)$_2$ were prepared according to published procedures.[2] The Pd(PhCN)$_2$Cl$_2$ was prepared by the method of Doyle et al.[4]

Preparation of [Ni(δ-HCQD)$_2$Ag]$_3$·2.5CHCl$_3$. To 3 mL of a $CHCl_3$ solution containing 0.05 g (0.11 mmol) of Ni(δ-HCQD)$_2$ was added approximately 5 mL of 0.05 M aqueous $AgNO_3$ solution. The two solution layers were mixed together by adding MeOH (15 mL) until a homogeneous solution was obtained. The resulting green solution was allowed to evaporate overnight at room temperature. After 24 h green needlelike crystals were obtained; yield 90%. IR (KBr): ν(C=N) 1615, 1560 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.20 (d), C4–H; 1.12 (s), 0.86 (s), 0.78 (s), Me. ^{13}C NMR ($CDCl_3$) (ppm): 153.76, 153.49, 147.42, 147.31, oxime C; 20.0, 17.35, 11.99, Me. UV-vis maxima ($CHCl_3$): 620 nm (53 cm^{-1} M^{-1}), 402 (1.2 × 10^3), 305 (1.5 × 10^4). Anal. Calcd for [Ni($C_{20}H_{29}N_4O_4$)Ag]$_3$·2.5CHCl$_3$: C, 38.22; H, 4.60; N, 8.56; Cl, 13.54; Ag, 16.48. Found: C, 37.94; H, 4.70; N, 8.45; Cl, 13.60; Ag, 17.13.

Preparation of [Pd(δ-HCQD)$_2$Ag]$_3$·2CHCl$_3$. Yellow crystals of [Pd(δ-HCQD)$_2$Ag]$_3$·2CHCl$_3$ were prepared by using the same pro-

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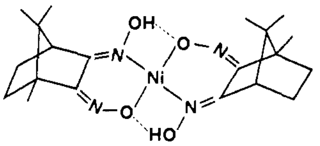

Figure 1. Structure of Ni(δ-HCQD)$_2$.

cedure as for [Ni(δ-HCQD)$_2$Ag]$_3$·2.5CHCl$_3$ substituting Pd(δ-HCQD)$_2$ for Ni(δ-HCQD)$_2$; yield 80%. IR (KBr): ν(C=N) 1605, 1550 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.31 (d), C4–H; 1.24 (s), 0.90 (s), 0.78 (s), Me. ^{13}C NMR (CDCl$_3$) (ppm): 153.70, 142.49, oxime C; 20.05, 17.40, 12.58, Me. UV-vis maxima (CHCl$_3$): 362 nm (1.8 × 10^3 cm^{-1} M^{-1}). Anal. Calcd for [Pd(C$_{20}$H$_{29}$N$_4$O$_4$)Ag]$_3$·2CHCl$_3$: C, 36.37; H, 4.39; N, 8.21; Cl, 10.39; Ag, 15.81. Found: C, 36.27; H, 4.54; N, 8.04; Cl, 7.22; Ag, 15.48.

Preparation of Ni(α-HCQD)$_2$Ag·0.5AgNO$_3$·H$_2$O. This complex was prepared in the same manner as [Ni(δ-HCQD)$_2$Ag]$_3$·2.5CHCl$_3$ substituting Ni(α-HCQD)$_2$ for Ni(δ-HCQD)$_2$; yield 90%. IR (KBr): ν(C=N) 1615, 1550 cm^{-1}. UV-vis maxima (CHCl$_3$): 402, 302 nm. Anal. Calcd for Ni(C$_{20}$H$_{29}$N$_4$O$_4$)Ag·0.5AgNO$_3$·H$_2$O: C, 36.44; H, 4.75; N, 9.57; Ag, 24.55. Found: C, 36.64; H, 4.47; N, 9.37; Ag, 24.62.

Preparation of Pd(α-HCQD)$_2$Ag·0.5AgNO$_3$. To 20 mL of MeOH containing 0.32 mmol of α-H$_2$CQD was added an equivalent amount of Et$_3$N (0.32 mmol), followed by 0.16 mmol of Pd(PhCN)$_2$Cl$_2$. After being stirred at 50° C for 2–3 h, the yellow solution was filtered and cooled to room temperature. Then aqueous AgNO$_3$ (0.05 M) was added until no further precipitation of AgCl was observed. The solution was then filtered into a flask containing 10 mL of CHCl$_3$. When the solution was allowed to stand overnight, the product Pd(α-HCQD)$_2$Ag·0.5AgNO$_3$ crystallized out as pale yellow microcrystals, yield 80%. IR (KBr): ν(C=N) 1600, 1550 cm^{-1}. UV-vis maximum (CHCl$_3$): 362 nm. Anal. Calcd for Pd(C$_{20}$H$_{29}$N$_4$O$_4$)Ag·0.5AgNO$_3$: C, 34.87; H, 4.25; N, 9.14; Ag, 23.49. Found: C, 34.98; H, 4.21; N, 9.42; Ag, 22.59.

Preparation of [Ni(δ-HCQD)$_2$(py)$_2$]·CHCl$_3$. This complex was prepared by dissolving 0.05 g (0.11 mmol) of Ni(δ-HCQD)$_2$ in 20 mL of H$_2$O/MeOH/CHCl$_3$ (1:3:1) to which 1 mL of pyridine (py) was added. After the solution was allowed to stand at room temperature for several days, green crystals of [Ni(δ-HCQD)$_2$(py)$_2$]·CHCl$_3$ were obtained; yield 80%. IR (KBr): ν(C=N) 1610, 1558 cm^{-1}. UV-vis maxima (CHCl$_3$): 614 nm (58 cm^{-1} M^{-1}), 296 (1.4 × 10^4). Λ (CH$_3$CN): 0.534 cm^2 Ω^{-1} M^{-1} at 25° C. Anal. Calcd for Ni(C$_{20}$H$_{29}$N$_4$O$_4$)(C$_5$H$_5$N)$_2$·CHCl$_3$: C, 51.23; H, 5.70; N, 11.57. Found: C, 51.26; H, 6.02; N, 11.71.

Crystal Data. [Ni(δ-HCQD)$_2$Ag]$_3$·2.5CHCl$_3$: mol wt 1832.40, orthorhombic $P2_12_12_1$, a = 15.990 (5) Å, b = 38.44 (1) Å, c = 13.437 (5) Å, V = 8260.97 Å^3, ρ_c = 1.474 g/cm^3, Z = 4, μ = 15.32 cm^{-1} for Mo Kα. [Pd(δ-HCQD)$_2$Ag]$_3$·2CHCl$_3$: mol wt 1945.62, orthorhombic $P2_12_12_1$, a = 16.110 (6) Å, b = 38.92 (1) Å, c = 13.393 (3) Å, V = 8395.55 Å^3, ρ_c = 1.540 g/cm^3, Z = 4, μ = 14.47 cm^{-1} for Mo Kα. The [Ni(δ-HCQD)$_2$Ag]$_3$·2.5CHCl$_3$ cluster will be referred to as Ni–Ag, while [Pd(δ-HCQD)$_2$Ag]$_3$·2CHCl$_3$ will be designated Pd–Ag in the discussion below.

A 0.36 × 0.19 × 0.16 mm single crystal of Ni–Ag and a 0.30 × 0.08 × 0.10 mm crystal of Pd–Ag were used in the collection of X-ray intensity data. In each case, 12–15 independent reflections taken from four preliminary ω-oscillation photographs at various χ and ϕ settings were input to the automatic indexing program ALICE.[5] The resulting reduced cell and reduced cell scalars indicated $P2_12_12_1$ (orthorhombic) symmetry in both cases. This was confirmed by inspection of axial ω-oscillation photographs which showed *mmm* symmetry in both Ni–Ag and Pd–Ag. The final lattice constants were obtained by using least-squares refinement based on the precise $\pm 2\theta$ measurement of 13 independent reflections with $|2\theta| > 20°$ for Ni–Ag and 15 independent reflections with $|2\theta| > 30°$ for Pd–Ag.

Collection and Reduction of X-ray Intensity Data. The data were collected at 25 °C with use of graphite-monochromated Mo Kα radiation on an automated four-circle diffractometer designed and built at the Ames Laboratory and previously described by Rohrbaugh and Jacobson.[6] All data (4412 reflections for Ni–Ag and 6524 reflections for Pd–Ag) within a 2θ sphere of 40° in the case of Ni–Ag and 60° in the case of Pd–Ag in the *hkl* octant were measured using an ω-step-scan technique.

As a general check on electronic and crystal stability, the intensities of three standard reflections were measured every 75 reflections. These standard reflections were not observed to vary significantly throughout the data collection period (~6 days) for the Pd–Ag complex but indicated considerable decay for the Ni–Ag complex in the last 1025 reflections. The decay as measured from the standard reflections was found to fit a quadratic polynomial by the least-squares method: $y(x) = 5979 + (-0.2615)x + (-0.0007267)x^2$. Subsequently all reflections after the first 3375 in the Ni–Ag complex were divided by $y(x)/y(0) = 1.0 + (-0.4374 \times 10^{-5})x + (-1.216 \times 10^{-7})x^2$ to account for the decay correction.

Examination of data revealed systematic absences of $h00$, $0k0$, $00l$ reflections for $h = 2n + 1$, $k = 2n + 1$, $l = 2n + 1$ in the Ni–Ag and Pd–Ag structures, thus uniquely defining the space group $P2_12_12_1$ in both cases. The intensity data were corrected for Lorentz and polarization effects. An absorption correction was applied to the data of the Pd–Ag complex. However, no absorption correction was applied to the Ni–Ag data because the crystal diffracted only out to 40° in 2θ and because the transmission factors were in the range 0.80 ± 0.09. The estimated error in each intensity was calculated by $\sigma_I^2 = C_T + K_tC_B + (0.03C_T)^2 + (0.03C_B)^2$, where C_T, K_t, and C_B represent the total count, a counting time factor, and background count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite-difference method.[7] Since only one octant of data was collected in each case, no averaging of data was required. While 3021 reflections with $I_0 > 3\sigma_I$ from Ni–Ag were retained for structural solution and refinement, 6112 reflections from Pd–Ag were retained.

Solution and Refinement of the Structures. The positions of the heavy atoms in the asymmetric unit were obtained from an analysis of a standard sharpened three-dimensional Patterson map.[7] The remaining nonhydrogen atoms were found by successive structure factor and electron density map calculations.[8] A block-matrix least-squares procedure[9] was used to refine the atomic positional parameters with anisotropic thermal parameters for the metal atoms and isotropic thermal parameters for the remaining nonhydrogen atoms to conventional discrepancy factors of $R = \sum||F_o| - |F_c||/\sum|F_o|| =$ 10.7 and 11.4 and weighted R values of 12.7 and 15.0 for the Ni–Ag and Pd–Ag structures, respectively, by using weights of $1/\sigma_F^2$. There were three possible solvent sites in both structures. The Pd–Ag structure indicated that all three sites had disordered CHCl$_3$ molecules. Although two of the solvent sites in the Ni–Ag structure also exhibited peaks corresponding to disordered CHCl$_3$ molecules, the third site contained much less electron density. Both structures contained less solvent than was indicated by the elemental analyses. This is believed to be due to some loss of solvent during data collection. The decay observed in the standard reflections, especially evident for the Ni–Ag crystal, would be consistent with ready solvent loss. Thermal and occupancy factors were estimated from successive electron density difference maps. In both structures, final electron density difference maps revealed no peaks larger than 1.0 e/Å^3. Hydrogen positions in the terminal methyl groups and in the bicyclic rings were calculated by using a 1.07 Å C–H bond distance and tetrahedral H–C–H angles in both Ni–Ag and Pd–Ag. They were included but not refined during the last least-squares refinement cycles. The scattering factors for nonhydrogen atoms were those of Hanson et al.,[10] modified by the real and imaginary parts of anomalous dispersion.[11] Scattering factors for Ni(II), Pd(II), and Ag(I) were those of Thomas and Umeda.[12]

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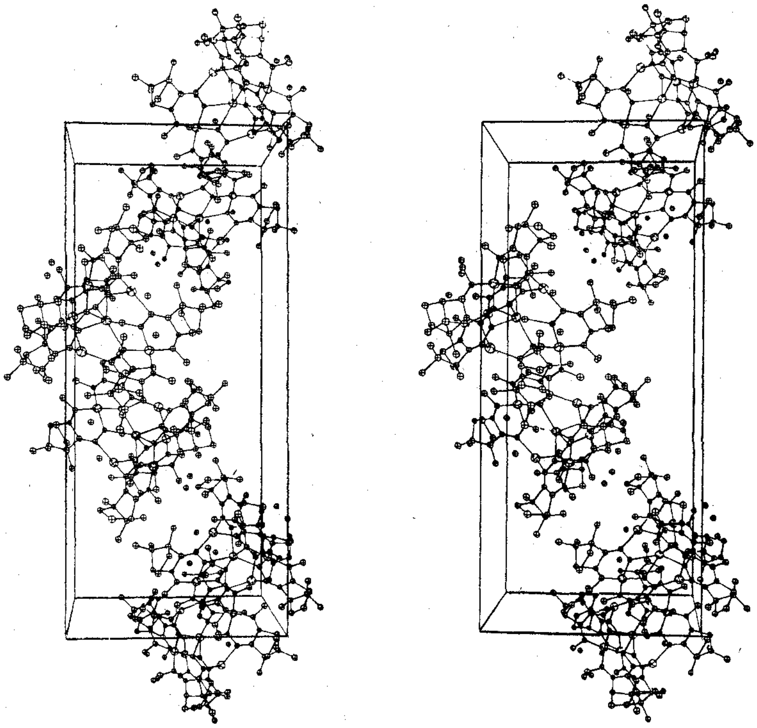

Figure 2. Stereoscopic view of the unit cell of $[Ni(\delta\text{-HCQD})_2Ag]_3 \cdot 2.5CHCl_3$ with the *a* axis vertical and the *b* axis horizontal.

Hydrogen scattering factors were those of Stewart et al.[13] Final positional and thermal parameters for Ni–Ag and Pd–Ag are listed in Tables I and II, respectively.

Results and Discussion

Description of the Structure $[Ni(\delta\text{-HCQD})_2Ag]_3 \cdot 2.5CHCl_3$, Ni–Ag. The unit cell (Figure 2) of Ni–Ag consists of four hexanuclear molecules with $CHCl_3$ molecules occupying interstitial sites. Each hexanuclear molecule (Figure 3) in turn consists of three individual $Ni(\delta\text{-HCQD})_2^-$ ligands coordinated to a linear chain of three silver atoms. The $\delta\text{-HCQD}^-$ ligands form two six-membered chelate rings with each of the three Ni(II) atoms. The observed coordination of the ligands to Ni via N and O rather than two N atoms was established previously in $Ni(\delta\text{-HCQD})_2$[1] and probably is caused by the bicyclic nature of the ligand which increases the size of the C–C–N angles and thus favors six-membered chelate ring formation. There are two types of Ag atoms in the cluster. Coordinated to the center Ag are six oxygen atoms, while there are three nitrogen atoms coordinated to each of the terminal silver atoms. Several interesting features of the structure are discussed below.

Coordination around Ni. While the crystal structure[1] of $Ni(\delta\text{-HCQD})_2$ was found to have *trans*-N_2O_2 square-planar coordination around Ni (Figure 1), the $\delta\text{-HCQD}^-$ ligands in Ni–Ag coordinate to the Ni with a *cis*-N_2O_2 geometry (Figure 3). Thus, the addition of Ag^+ to $Ni(\delta\text{-HCQD})_2$ has caused one ligand in $Ni(\delta\text{-HCQD})_2$ to rotate such that the structure around the Ni changes from *trans*-N_2O_2 to *cis*-N_2O_2.

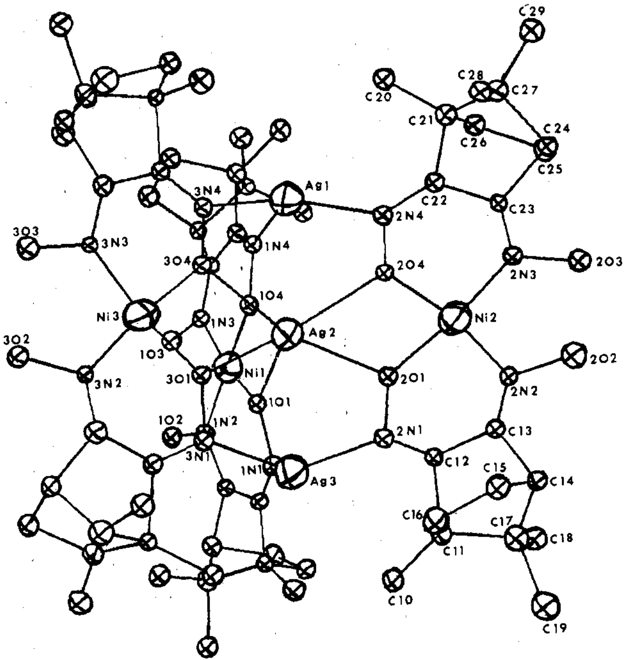

Figure 3. Molecular structure of $[Ni(\delta\text{-HCQD})_2Ag]_3$ with 50% probability ellipsoids for heavy atoms but 10% for light atoms. For clarity only the C atoms of the Ni2 unit are labeled but the adopted numbering scheme is also applied to the other two units.

The important bond distances and bond angles of the three $Ni(\delta\text{-HCQD})_2^-$ units in Ni–Ag are summarized in Tables III and IV. The average Ni–N distance of 1.86 (4) Å is comparable to 1.855 (3) Å reported in the $Ni(\delta\text{-HCQD})_2$ complex.[1] However, the average Ni–O distance of 1.87 (3) Å is longer than the 1.830 (3) Å observed in $Ni(\delta\text{-HCQD})_2$. This lengthening is presumably due to coordination of the Ag(I) to these O atoms. Also such coordination seems to affect the O4–Ni–O1 angles (75.9 (1), 77.2 (1), and 80.5 (1)°) so that they are consistently smaller than the other angles, O4–Ni–N3, N3–Ni–N2, and N2–Ni–O1, which are all greater than 90° in the three nickel anion ligands. The distances of the Ni atoms from the least-squares planes defined by Ni–O1–O4–N2–N3 are small, being only 0.04, 0.006, and 0.01 Å for the three units. The average C—C (1.53 Å), C═N (1.28 Å), and N—O (1.38 Å) distances of the ligands correspond well with those observed in the structures of $Ni(\delta\text{-HCQD})_2$[1] and $\gamma\text{-}H_2CQD$.[14]

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Table I. Final Atomic Parameters of the Ni–Ag Structure[a]

(a) Final Positional Parameters and Isotropic Thermal Parameters (B) of the Light Atoms

	x	y	z	B, Å^2		x	y	z	B, Å^2
Ag1	0.2093 (2)	0.1705 (1)	−0.0952 (3)		2C21	−0.0207 (34)	0.1459 (14)	−0.0266 (41)	6.8 (14)
Ag2	0.3188 (2)	0.1124 (1)	−0.1801 (3)		2C22	0.0456 (30)	0.1213 (13)	−0.0818 (38)	5.7 (12)
Ag3	0.4230 (2)	0.0530 (1)	−0.2658 (3)		2C23	−0.0004 (26)	0.0882 (11)	−0.0871 (33)	4.1 (10)
Ni1	0.4713 (4)	0.1239 (2)	0.0159 (5)		2C24	−0.0959 (29)	0.0944 (11)	−0.0466 (35)	5.0 (11)
Ni2	0.1326 (4)	0.0568 (2)	−0.1905 (5)		2C25	−0.0732 (38)	0.0948 (14)	0.0663 (45)	8.5 (16)
Ni3	0.3937 (4)	0.1704 (2)	−0.3759 (4)		2C26	−0.0207 (35)	0.1328 (14)	0.0836 (43)	6.8 (14)
1O1	0.4422 (18)	0.0951 (7)	−0.0944 (23)	5.0 (7)	2C27	−0.1014 (34)	0.1357 (13)	−0.0798 (41)	6.1 (14)
1O2	0.6331 (19)	0.1170 (8)	0.1003 (25)	6.2 (8)	2C28	−0.1003 (32)	0.1389 (12)	−0.1850 (39)	6.2 (13)
1O3	0.5524 (21)	0.1625 (9)	0.1716 (26)	7.4 (9)	2C29	−0.1834 (37)	0.1483 (15)	−0.0230 (45)	8.5 (16)
1O4	0.3700 (19)	0.1418 (8)	−0.0279 (23)	5.3 (7)	3O1	0.4007 (18)	0.1247 (7)	−0.3379 (21)	4.8 (7)
1N1	0.4795 (23)	0.0620 (10)	−0.1228 (29)	5.4 (9)	3O2	0.5043 (19)	0.1934 (8)	−0.5306 (24)	5.7 (8)
1N2	0.5747 (25)	0.1038 (9)	0.0399 (29)	5.6 (9)	3O3	0.4149 (22)	0.2343 (8)	−0.4723 (25)	6.8 (8)
1N3	0.4795 (23)	0.1588 (9)	0.1187 (29)	5.0 (9)	3O4	0.3154 (18)	0.1706 (8)	−0.2693 (22)	5.2 (7)
1N4	0.3152 (22)	0.1676 (9)	0.0088 (26)	5.2 (8)	3N1	0.4524 (22)	0.0974 (9)	−0.3632 (28)	5.2 (9)
1C10	0.5666 (37)	0.0005 (15)	−0.1742 (46)	7.9 (16)	3N2	0.4751 (20)	0.1645 (8)	−0.4718 (24)	3.7 (8)
1C11	0.5987 (27)	0.0218 (11)	−0.0934 (34)	5.0 (10)	3N3	0.3720 (19)	0.2162 (8)	−0.4004 (24)	3.2 (7)
1C12	0.5451 (29)	0.0515 (13)	−0.0769 (36)	4.9 (12)	3N4	0.2671 (23)	0.1947 (10)	−0.2356 (28)	4.7 (9)
1C13	0.5972 (27)	0.0710 (11)	0.0084 (32)	4.6 (10)	3C10	0.5395 (34)	0.0397 (14)	−0.4584 (42)	6.7 (14)
1C14	0.6786 (33)	0.0491 (14)	0.0180 (40)	6.3 (13)	3C11	0.5639 (28)	0.0762 (11)	−0.4849 (33)	4.5 (10)
1C15	0.6392 (35)	0.0198 (14)	0.0848 (44)	7.7 (15)	3C12	0.4991 (28)	0.1057 (12)	−0.4437 (36)	4.9 (11)
1C16	0.5909 (32)	0.0020 (13)	0.0047 (39)	6.4 (13)	3C13	0.5107 (36)	0.1379 (14)	−0.4916 (43)	6.5 (15)
1C17	0.6834 (38)	0.0359 (15)	−0.0830 (48)	7.5 (16)	3C14	0.5769 (30)	0.1313 (11)	−0.5723 (34)	5.2 (11)
1C18	0.7012 (34)	0.0579 (14)	−0.1699 (43)	7.3 (14)	3C15	0.6617 (31)	0.1254 (13)	−0.5082 (38)	6.1 (13)
1C19	0.7529 (33)	0.0062 (13)	−0.0904 (40)	6.9 (13)	3C16	0.6442 (33)	0.0913 (14)	−0.4515 (41)	5.9 (14)
1C20	0.1959 (34)	0.2097 (14)	0.1276 (42)	6.9 (14)	3C17	0.5593 (36)	0.0953 (14)	−0.5972 (46)	7.7 (15)
1C21	0.2937 (33)	0.2093 (13)	0.1471 (39)	6.3 (13)	3C18	0.4772 (33)	0.0913 (13)	−0.6463 (40)	7.4 (14)
1C22	0.3422 (28)	0.1816 (12)	0.0903 (36)	5.9 (11)	3C19	0.6206 (32)	0.0758 (13)	−0.6605 (39)	6.4 (13)
1C23	0.4188 (27)	0.1793 (10)	0.1414 (30)	4.3 (10)	3C20	0.1713 (38)	0.2504 (16)	−0.1438 (45)	9.4 (17)
1C24	0.4175 (31)	0.2034 (12)	0.2243 (36)	5.2 (12)	3C21	0.2108 (26)	0.2565 (10)	−0.2434 (32)	3.9 (10)
1C25	0.4248 (35)	0.2382 (14)	0.1791 (43)	8.4 (14)	3C22	0.2678 (27)	0.2237 (11)	−0.2734 (34)	4.9 (11)
1C26	0.3418 (29)	0.2432 (12)	0.1119 (37)	5.5 (12)	3C23	0.3136 (30)	0.2354 (12)	−0.3633 (36)	5.6 (12)
1C27	0.3221 (28)	0.2037 (12)	0.2568 (34)	4.8 (11)	3C24	0.2921 (30)	0.2748 (12)	−0.3695 (37)	5.6 (12)
1C28	0.2953 (32)	0.1685 (14)	0.2991 (39)	6.4 (13)	3C25	0.2035 (41)	0.2728 (16)	−0.4115 (52)	9.8 (18)
1C29	0.2920 (42)	0.2307 (17)	0.3259 (53)	9.4 (19)	3C26	0.1468 (30)	0.2599 (12)	−0.3211 (38)	5.9 (12)
2O1	0.2441 (17)	0.0572 (7)	−0.2207 (20)	4.2 (6)	3C27	0.2739 (33)	0.2838 (13)	−0.2640 (41)	6.6 (14)
2O2	0.0350 (24)	0.0006 (10)	−0.2628 (30)	7.5 (10)	3C28	0.3526 (36)	0.2812 (15)	−0.1931 (45)	7.8 (15)
2O3	−0.0342 (22)	0.0353 (9)	−0.1395 (27)	8.4 (10)	3C29	0.2323 (33)	0.3215 (14)	−0.2598 (42)	7.4 (14)
2O4	0.1677 (16)	0.1016 (7)	−0.1442 (20)	4.5 (7)	1Cl1[b] (0.4)[c]	0.5515 (27)	0.2176 (12)	−0.2676 (34)	7.0
2N1	0.2948 (22)	0.0339 (9)	−0.2699 (28)	5.2 (9)	1Cl2 (0.4)	0.6120 (22)	0.1534 (9)	−0.2148 (26)	7.0
2N2	0.1167 (20)	0.0143 (8)	−0.2601 (25)	5.5 (9)	1Cl3 (0.4)	0.5810 (24)	0.2004 (9)	−0.0690 (28)	7.0
2N3	0.0271 (23)	0.0614 (10)	−0.1374 (28)	3.9 (8)	1Cl4 (0.25)	0.6242 (31)	0.1758 (13)	−0.1071 (40)	7.0
2N4	0.1224 (23)	0.1269 (9)	−0.1081 (29)	4.9 (9)	1Cl5 (0.25)	0.5138 (32)	0.2174 (13)	−0.0980 (41)	7.0
2C10	0.3948 (33)	−0.0268 (13)	−0.3559 (39)	6.3 (13)	1Cl6 (0.25)	0.5787 (34)	0.2081 (14)	−0.2846 (40)	7.0
2C11	0.2986 (31)	−0.0229 (12)	−0.3757 (38)	6.0 (12)	1CS1 (0.4)	0.5533 (73)	0.1934 (30)	−0.1930 (95)	7.0
2C12	0.2535 (28)	0.0089 (11)	−0.3081 (36)	4.5 (11)	1CS2 (0.25)	0.5731 (132)	0.2042 (55)	−0.2743 (167)	7.0
2C13	0.1661 (28)	−0.0011 (12)	−0.3125 (38)	5.0 (11)	2Cl1 (0.4)	0.2510 (21)	0.1022 (9)	−0.4902 (26)	7.0
2C14	0.1602 (30)	−0.0351 (12)	−0.3694 (37)	5.3 (12)	2Cl2 (0.4)	0.1438 (21)	0.1527 (9)	−0.4040 (26)	7.0
2C15	0.1790 (34)	−0.0217 (14)	−0.4662 (42)	7.6 (14)	2Cl3 (0.4)	0.1095 (21)	0.0815 (9)	−0.4340 (26)	7.0
2C16	0.2642 (39)	−0.0143 (15)	−0.4752 (48)	8.7 (17)	2Cl4 (0.25)	0.0774 (34)	0.1022 (13)	−0.3785 (41)	7.0
2C17	0.2388 (37)	−0.0522 (16)	−0.3372 (46)	8.4 (16)	2Cl5 (0.25)	0.2171 (37)	0.0922 (15)	−0.4421 (45)	7.0
2C18	0.2574 (42)	−0.0868 (16)	−0.4012 (53)	9.2 (18)	2Cl6 (0.25)	0.1878 (36)	0.1528 (14)	−0.4734 (43)	7.0
2C19	0.2474 (34)	−0.0628 (14)	−0.2316 (42)	7.4 (15)	2CS2 (0.25)	0.1883 (121)	0.1171 (51)	−0.4164 (152)	7.0
2C20	0.0064 (33)	0.1843 (13)	−0.0426 (41)	6.4 (14)	1OS (0.55)	0.5187 (37)	0.3270 (16)	−0.3466 (44)	7.0

(b) Anisotropic Thermal Parameters (×10^5) of the Heavy Atoms[d]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag1	396 (18)	69 (3)	805 (29)	3 (6)	−48 (20)	18 (9)	Ni1	390 (30)	58 (5)	709 (47)	−6 (11)	8 (34)	−2 (14)
Ag2	400 (16)	58 (3)	718 (26)	0 (6)	24 (19)	32 (8)	Ni2	404 (30)	55 (5)	676 (45)	−7 (10)	−44 (33)	18 (14)
Ag3	411 (17)	67 (3)	793 (29)	0 (7)	−41 (21)	24 (8)	Ni3	429 (31)	57 (5)	633 (44)	13 (11)	−55 (31)	−2 (14)

[a] In all tables, estimated standard deviations are given in parentheses. [b] Only 1.3 $CHCl_3$ rather than 2.5 $CHCl_3$ as indicated by elemental analyses was observed on an electron density difference map. [c] Multiplier used. [d] The β_{ij} are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Since intramolecular H bonding is of interest in almost all metal dioxime complexes, it is worthwhile to mention the O2–O3 distances (2.38 (5), 2.40 (5), and 2.27 (4) Å) for the three nickel anion complexes. They are comparable to the 2.40 Å reported for the dimethylglyoximato complex Ni(HDMG)$_2$[15] and other related oxime metal complexes.[16]

Since the O2–O3 bond distances are not equal in the three Ni(δ-HCQD)$_2^-$ ligands, they appear to be affected by crys-

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Table II. Final Atomic Parameters of the Pd-Ag Structure

(a) Final Positional Parameters and Isotropic Thermal Parameters (*B*) of the Light Atoms

	x	y	z	B, Å^2		x	y	z	B, Å^2
Ag1	0.29459 (13)	0.32877 (5)	0.40075 (20)		2C20	0.4863 (20)	0.3178 (8)	0.4807 (22)	5.9 (7)
Ag2	0.18500 (12)	0.38870 (5)	0.30904 (19)		2C21	0.5108 (20)	0.3544 (7)	0.4792 (26)	5.2 (7)
Ag3	0.07899 (13)	0.44983 (5)	0.21672 (20)		2C22	0.4556 (18)	0.3788 (7)	0.4193 (24)	5.0 (6)
Pd1	0.02627 (13)	0.37629 (5)	0.49885 (20)		2C23	0.5007 (16)	0.4105 (6)	0.4028 (23)	4.4 (6)
Pd2	0.37097 (12)	0.44287 (4)	0.29997 (19)		2C24	0.5904 (22)	0.4043 (9)	0.4445 (31)	6.1 (8)
Pd3	0.10885 (13)	0.33064 (5)	0.11501 (19)		2C25	0.5799 (26)	0.4074 (11)	0.5594 (37)	9.3 (11)
1O1	0.0538 (11)	0.4079 (5)	0.3827 (17)	4.5 (4)	2C26	0.5201 (23)	0.3698 (9)	0.5794 (31)	7.5 (11)
1O2	−0.1388 (12)	0.3859 (5)	0.5920 (17)	5.7 (4)	2C27	0.5891 (17)	0.3652 (7)	0.4299 (23)	5.5 (6)
1O3	−0.0548 (13)	0.3389 (5)	0.6592 (18)	6.1 (5)	2C28	0.6009 (24)	0.3537 (9)	0.3285 (33)	6.4 (9)
1O4	0.1379 (11)	0.3573 (4)	0.4567 (15)	4.6 (4)	2C29	0.6710 (21)	0.3482 (8)	0.4723 (29)	6.6 (8)
1N1	0.0174 (14)	0.4387 (6)	0.3597 (20)	4.4 (5)	3O1	0.1044 (11)	0.3797 (4)	0.1497 (14)	4.3 (4)
1N2	−0.0812 (15)	0.4000 (6)	0.5254 (20)	5.2 (5)	3O2	−0.0055 (12)	0.3075 (4)	−0.0418 (16)	4.8 (4)
1N3	0.0151 (15)	0.3414 (6)	0.6090 (21)	4.8 (5)	3O3	0.0807 (13)	0.2640 (5)	0.0248 (17)	5.8 (4)
1N4	0.1784 (13)	0.3339 (5)	0.5103 (17)	3.8 (4)	3O4	0.1923 (12)	0.3334 (5)	0.2219 (16)	5.4 (4)
1C10	−0.0710 (24)	0.5017 (10)	0.3055 (34)	7.1 (9)	3N1	0.0535 (15)	0.4037 (6)	0.1110 (22)	5.0 (6)
1C11	−0.1012 (22)	0.4808 (9)	0.3946 (31)	6.9 (8)	3N2	0.0226 (14)	0.3360 (5)	0.0113 (19)	4.6 (5)
1C12	−0.0516 (17)	0.4463 (7)	0.4056 (24)	4.8 (6)	3N3	0.1271 (14)	0.2803 (5)	0.0880 (19)	4.8 (5)
1C13	−0.0987 (17)	0.4291 (7)	0.4849 (24)	5.3 (6)	3N4	0.2423 (15)	0.3059 (6)	0.2600 (20)	4.7 (5)
1C14	−0.1820 (19)	0.4494 (8)	0.4961 (27)	5.2 (7)	3C10	−0.0294 (21)	0.4603 (8)	−0.0069 (29)	6.1 (8)
1C15	−0.1500 (18)	0.4783 (7)	0.5686 (26)	5.9 (6)	3C11	−0.0523 (19)	0.4229 (8)	−0.0055 (27)	5.5 (7)
1C16	−0.1018 (24)	0.4983 (10)	0.4895 (34)	6.0 (9)	3C12	0.0084 (17)	0.3964 (7)	0.0450 (24)	3.8 (6)
1C17	−0.1916 (17)	0.4646 (7)	0.3893 (24)	5.1 (6)	3C13	−0.0131 (18)	0.3631 (7)	−0.0104 (25)	4.7 (6)
1C18	−0.2584 (28)	0.4938 (10)	0.3913 (35)	7.9 (9)	3C14	−0.0791 (19)	0.3680 (7)	−0.0824 (25)	5.2 (6)
1C19	−0.2074 (21)	0.4408 (8)	0.3138 (30)	5.9 (8)	3C15	−0.1574 (21)	0.3756 (8)	−0.0252 (28)	7.3 (8)
1C20	0.2931 (21)	0.2897 (8)	0.6230 (28)	6.2 (7)	3C16	−0.1415 (24)	0.4096 (10)	0.0297 (35)	6.1 (11)
1C21	0.1966 (19)	0.2900 (8)	0.6360 (27)	5.5 (7)	3C17	−0.0594 (19)	0.4078 (8)	−0.1209 (28)	5.4 (7)
1C22	0.1513 (15)	0.3186 (6)	0.5801 (21)	3.8 (5)	3C18	−0.1196 (22)	0.4251 (9)	−0.1782 (31)	7.4 (8)
1C23	0.0704 (17)	0.3194 (6)	0.6344 (22)	3.7 (6)	3C19	0.0282 (24)	0.4066 (9)	−0.1674 (33)	5.8 (9)
1C24	0.0667 (19)	0.2956 (7)	0.7120 (26)	5.6 (7)	3C20	0.3304 (23)	0.2486 (9)	0.3504 (32)	6.2 (8)
1C25	0.0635 (25)	0.2599 (10)	0.6574 (33)	7.9 (9)	3C21	0.2868 (20)	0.2450 (8)	0.2503 (27)	6.4 (7)
1C26	0.1491 (23)	0.2557 (9)	0.6086 (33)	6.6 (11)	3C22	0.2355 (15)	0.2751 (6)	0.2164 (21)	4.0 (5)
1C27	0.1582 (20)	0.2966 (8)	0.7466 (28)	6.8 (7)	3C23	0.1806 (20)	0.2640 (8)	0.1393 (27)	5.3 (7)
1C28	0.1851 (28)	0.2655 (11)	0.8196 (40)	9.1 (10)	3C24	0.2027 (21)	0.2254 (8)	0.1267 (30)	6.7 (7)
1C29	0.1890 (25)	0.3314 (10)	0.7868 (35)	8.6 (10)	3C25	0.2923 (24)	0.2262 (9)	0.0765 (32)	8.7 (9)
2O1	0.2493 (11)	0.4438 (4)	0.2654 (14)	4.2 (3)	3C26	0.3535 (28)	0.2368 (10)	0.1631 (39)	8.9 (11)
2O2	0.4695 (14)	0.5007 (6)	0.2286 (19)	6.5 (5)	3C27	0.2208 (17)	0.2163 (7)	0.2324 (23)	5.4 (6)
2O3	0.5397 (14)	0.4623 (5)	0.3444 (19)	6.4 (5)	3C28	0.1461 (22)	0.2176 (9)	0.3047 (32)	6.6 (8)
2O4	0.3324 (11)	0.3972 (4)	0.3522 (15)	4.3 (4)	3C29	0.2689 (26)	0.1818 (10)	0.2386 (36)	9.1 (11)
2N1	0.2095 (14)	0.4679 (5)	0.2114 (20)	4.4 (5)	C1 (0.5)[a]	0.4331 (58)	0.1914 (23)	0.7051 (83)	7.0
2N2	0.3946 (14)	0.4872 (5)	0.2307 (19)	5.2 (5)	C2 (0.5)	0.0674 (101)	0.1194 (38)	0.0101 (134)	7.0
2N3	0.4820 (14)	0.4380 (5)	0.3530 (20)	4.6 (5)	C3 (0.5)	0.3183 (99)	0.3863 (39)	0.0533 (132)	7.0
2N4	0.3833 (14)	0.3734 (5)	0.3950 (19)	4.6 (5)	1Cl1[b] (0.3)	0.3849 (26)	0.1535 (10)	0.7298 (35)	7.0
2C10	0.1141 (20)	0.5273 (8)	0.1258 (28)	6.3 (7)	1Cl2 (0.3)	0.4417 (26)	0.2198 (10)	0.7784 (36)	7.0
2C11	0.2009 (22)	0.5229 (9)	0.1225 (31)	7.6 (8)	1Cl3 (0.3)	0.4131 (27)	0.2016 (10)	0.5840 (35)	7.0
2C12	0.2487 (18)	0.4946 (7)	0.1793 (22)	3.3 (6)	1Cl4 (0.2)	0.4698 (39)	0.2153 (15)	0.6025 (54)	7.0
2C13	0.3384 (17)	0.5032 (7)	0.1835 (24)	4.4 (6)	1Cl5 (0.2)	0.4110 (39)	0.2101 (15)	0.7906 (55)	7.0
2C14	0.3457 (19)	0.5374 (7)	0.1285 (27)	5.1 (7)	1Cl6 (0.2)	0.3655 (39)	0.1840 (16)	0.6142 (54)	7.0
2C15	0.3389 (23)	0.5248 (9)	0.0164 (33)	9.1 (9)	2Cl1 (0.3)	0.1124 (26)	0.1054 (10)	0.0956 (36)	7.0
2C16	0.2388 (26)	0.5142 (9)	0.0145 (36)	8.4 (11)	2Cl2 (0.3)	0.1146 (26)	0.1545 (10)	0.9719 (35)	7.0
2C17	0.2665 (19)	0.5540 (7)	0.1484 (26)	5.0 (7)	2Cl3 (0.3)	0.1121 (25)	0.0879 (10)	0.9116 (36)	7.0
2C18	0.2593 (21)	0.5650 (8)	0.2586 (29)	8.0 (8)	3Cl1 (0.3)	0.3716 (27)	0.4213 (10)	0.0355 (36)	7.0
2C19	0.2433 (27)	0.5889 (10)	0.0930 (40)	9.2 (11)	3Cl2 (0.3)	0.3964 (26)	0.3616 (10)	0.1439 (36)	7.0
					3Cl3 (0.3)	0.2984 (27)	0.3633 (10)	−0.0138 (36)	7.0

(b) Anisotropic Thermal Parameters (×10^4) of the Heavy Atoms[c]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag1	37.0 (9)	6.5 (1)	80.2 (18)	−0.3 (3)	−3.7 (12)	3.0 (5)	Pd1	33.5 (8)	5.6 (1)	70.2 (16)	−2.1 (3)	−3.4 (11)	1.9 (4)
Ag2	35.2 (8)	5.8 (1)	71.8 (16)	−1.3 (3)	−2.9 (11)	7.9 (4)	Pd2	34.4 (9)	6.6 (1)	67.9 (16)	−0.5 (3)	5.0 (11)	0.3 (5)
Ag3	35.2 (8)	6.1 (1)	80.3 (19)	−0.9 (3)	−5.3 (11)	2.7 (5)	Pd3	41.4 (9)	6.1 (1)	64.2 (16)	0.1 (3)	−6.0 (11)	−0.8 (5)

[a] Multiplier used. [b] Only 1.1 $CHCl_3$ rather than 2 $CHCl_3$ as indicated by elemental analyses was observed on an electron density difference map. [c] The β_{ij} are defined by $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

tal-packing forces, which may also be the reason for the different Ag–O and Ag–N bond lengths in the three Ni(δ-HCQD)$_2^-$ units.

Configuration of the Metal Cluster. The geometry of the metal atoms in the molecule can be described best as a trigonal bipyramid (Tables V and VI) as shown in Figure 4. The deviation of Ag2 from the least-squares plane defined by Ni1–Ni2–Ni3–Ag2 is only 0.004 Å. The Ag1–Ag2–Ag3 chain is almost linear 178.1 (2)°. The angle between the Ag1–Ag2–Ag3 line and the Ni1–Ni2–Ni3 least-squares plane is 89.7°, indicating that the chain of silver atoms is nearly perpendicular to the plane.

It is worthwhile to note that Ag1 and Ag3 are about equidistant (~4.7 Å) from the three nickel atoms. However, they are too far for direct interaction. The center Ag2 is closer to the nickel atoms, about 3.6 Å away, but is still too far for M–M interactions to occur. The distances between the nickel atoms are listed in Table V with Ni1 and Ni3 closer to each other. Most interesting are the Ag1–Ag2 (3.056 (5) Å) and Ag2–Ag3 (3.052 (5) Å) distances. By comparison, the Ag–Ag

Table III.[a] Interatomic Distances (Å) for the Ni-Ag and Pd-Ag Structures

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
Ag1-N4	2.20 (4)	2.18 (4)	2.30 (4)	2.39 (2)	2.25 (2)	2.25 (3)
Ag1-O4	2.94 (3)	2.81 (3)	2.89 (3)	2.86 (2)	2.81 (2)	2.91 (2)
Ag2-O4	2.48 (3)	2.50 (3)	2.54 (3)	2.44 (2)	2.47 (2)	2.45 (2)
Ag2-O1	2.38 (3)	2.50 (3)	2.54 (3)	2.45 (2)	2.45 (2)	2.45 (2)
Ag3-O1	2.83 (3)	2.93 (3)	2.94 (3)	2.79 (2)	2.83 (2)	2.90 (2)
Ag3-N1	2.15 (4)	2.18 (4)	2.20 (4)	2.20 (3)	2.22 (2)	2.32 (3)
M[b]-O1	1.91 (3)	1.83 (3)	1.83 (3)	2.03 (2)	2.01 (2)	1.97 (2)
M-O4	1.86 (3)	1.92 (3)	1.90 (3)	2.02 (2)	2.01 (2)	1.97 (2)
M-N2	1.85 (4)	1.90 (3)	1.85 (3)	1.99 (2)	2.00 (2)	1.98 (2)
M-N3	1.93 (4)	1.84 (4)	1.82 (3)	2.01 (3)	1.93 (2)	2.02 (2)
O2-O3	2.38 (5)	2.40 (5)	2.26 (4)	2.45 (3)	2.43 (3)	2.36 (3)
O1-O4	2.31 (4)	2.34 (4)	2.41 (4)	2.59 (2)	2.54 (2)	2.49 (3)

[a] Selection from the complete table which is available as supplementary material. [b] Corresponds to the metal atom labeled on the top of each column.

Table IV.[a] Bond Angles (Deg) for the Ni-Ag and Pd-Ag Structures

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
O1-Ag2-O4	56.9 (10)	55.8 (9)	56.8 (9)	63.8 (6)	62.1 (6)	60.0 (6)
Ag2-O4-M[b]	112.4 (14)	111.7 (12)	109.7 (13)	108.6 (7)	109.6 (8)	111.2 (8)
Ag2-O1-M	114.6 (13)	115.2 (13)	112.3 (13)	108.2 (7)	109.9 (7)	108.4 (7)
O1-M-O4	75.9 (13)	77.2 (12)	80.5 (13)	79.2 (7)	78.2 (7)	78.4 (8)
O1-M-N2	96.4 (15)	91.6 (13)	91.9 (13)	92.6 (9)	93.6 (8)	92.1 (8)
O4-M-N3	91.6 (15)	93.2 (14)	90.4 (14)	92.2 (9)	94.1 (9)	94.9 (9)
N2-M-N3	96.0 (16)	98.7 (16)	97.3 (14)	96.0 (10)	94.5 (10)	94.6 (9)
O1-M-N3	167.4 (14)	168.3 (15)	170.7 (15)	171.4 (9)	170.5 (9)	172.9 (9)
O4-M-N2	171.3 (16)	166.5 (13)	172.0 (14)	172.0 (9)	170.4 (9)	170.6 (8)

[a] Selection from the complete table which is available as supplementary material. [b] Corresponds to the metal atom labeled on the top of each column.

Table V.[a] Distances between Heavy Atoms (Å)

Ni-Ag		Pd-Ag	
Ni1-Ni2	6.609 (9)	Pd1-Pd2	6.682 (3)
Ni1-Ni3	5.697 (9)	Pd2-Pd3	6.561 (3)
Ni2-Ni3	6.535 (10)	Pd1-Pd3	5.600 (4)
Ag1-Ag2	3.059 (5)	Ag1-Ag2	3.173 (3)
Ag2-Ag3	3.052 (7)	Ag2-Ag3	3.179 (3)
Ag2-Ni1	3.616 (7)	Ag2-Pd1	3.638 (3)
Ag2-Ni2	3.668 (8)	Ag2-Pd2	3.666 (3)
Ag2-Ni3	3.651 (8)	Ag2-Pd3	3.656 (3)

[a] Selection from the complete table which is available as supplementary material.

Table VI.[a] Related Angles (Deg) for the M_3Ag_3 Clusters

	Ni_3Ag_3	Pd_3Ag_3
Ag1-Ag2-Ag3	178.1 (2)	178.65 (4)
M[b]1-Ag2-M2	130.3 (2)	132.38 (9)
M1-Ag2-M3	103.2 (2)	100.29 (6)
M2-Ag2-M3	126.5 (2)	127.32 (8)

[a] Selection from the complete table which is available as supplementary material. [b] Represents Ni in column 2 and Pd in column 3.

distance in metallic silver is 2.89 Å.[17] Since a Ni-Ni distance of 3.25 Å is sufficient to indicate M-M interaction in the stacked $\mathrm{Ni(HDMG)_2}$[15] complex, it seems likely that there are interactions between the Ag atoms in the Ni-Ag cluster. The tendency of Ag(I) ions to form linear bonds may also contribute to the linear arrangement of the atoms.

Coordination around Ag. The Ag2 atom in the center of the chain is also coordinated to six O atoms of three $\mathrm{Ni}(\delta\text{-HCQD})_2^-$ units which act as bidentate ligands coordinating to Ag2 via their O1 and O4 oxime oxygen atoms, forming three four-membered chelate rings around Ag2 (Figure 3).

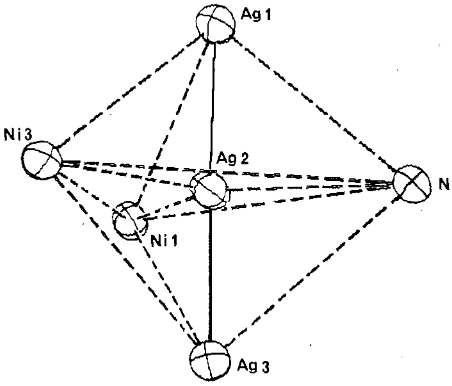

Figure 4. The trigonal bipyramid arrangement of the metal atoms in Ni-Ag.

The average Ag-O bond length is 2.49 (3) Å, well within the range of Ag-O bonds (2.15-2.88 Å) reported in the literature.[18-21] The three $\mathrm{Ni}(\delta\text{-HCQD})_2^-$ are not arranged symmetrically around Ag2 at 120° angles with respect to each other, but rather the dihedral angles formed between the three least-squares planes Ag2-1O4-Ni1-1O1, Ag2-2O4-Ni2-2O1 and Ag2-3O4-Ni3-3O1 are 130.2, 126.7, and 104.3°, respectively.

In contrast to Ag2, only N atoms (N1 or N4) from the $\mathrm{Ni}(\delta\text{-HCQD})_2^-$ ligands are coordinated to Ag1 and Ag3 to give a trigonal-pyramidal configuration in each case (Figure 3). The average Ag-N bond length is 2.20 (4) Å, comparable to other Ag-N bonds (2.11-2.51 Å) reported in the literature.[19-23] The oxime oxygen atoms O1 and O4 are too far

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(>2.8 Å) from Ag1 or Ag3 to form Ag–O bonds. The distances of Ag1 and Ag3 from the least-squares planes defined by 1N4–2N4–3N4 and 1N1–2N1–3N1, respectively, are 0.52 Å in both cases.

Within the unit cell (Figure 2) of Ni–Ag, no intermolecular H bonding is observed. However, molecules tend to pair up through van der Waals interactions between molecules along the twofold screw parallel to the *c* axis. There are also two sites for $CHCl_3$ near each hexanuclear molecule. The distances between the $[Ni(\delta\text{-HCQD})_2Ag]_3$ molecules and solvent sites (>3.4 Å) indicate interactions of only the van der Waals type.

Description of the Structure $[Pd(\delta\text{-HCQD})_2Ag]_3 \cdot 2CHCl_3$, Pd–Ag. A single crystal of the Pd–Ag complex prepared by adding aqueous $AgNO_3$ to a MeOH/$CHCl_3$ solution of $Pd(\delta\text{-HCQD})_2$ was chosen for the X-ray structural study. The results of that study showed that Pd–Ag has the same structure as Ni–Ag with $Pd(\delta\text{-HCQD})_2^-$ units acting as multidentate ligands. The average Pd–N bond length is 1.99 (2) Å, which corresponds well with literature values (1.96–2.03 Å) for palladium oxime complexes.[15,16a,24,25] The average Pd–O bond distance of 2.00 (2) Å is also comparable to those (2.00–2.03 Å) observed in other palladium oxime compounds.[24] While the average Ag–O (2.45 (2) Å) and Ag–N (2.27 (3) Å) bond distances are comparable to those of the Ni–Ag structure, the distances between Ag1–Ag2 (3.173 (3) Å) and Ag2–Ag3 (3.179 (3) Å) are significantly longer. This arises from the larger size of the Pd(II) ions which move the $\delta\text{-HCQD}^-$ ligands further away from each other in $Pd(\delta\text{-HCQD})_2^-$ as compared to $Ni(\delta\text{-HCQD})_2^-$, resulting in longer Ag–Ag distances (~3.17 Å). The Ag1–Ag2–Ag3 angle is almost linear, 178.6 (4)° (Table VI), and the angle between the Ag chain and the least-squares plane defined by Pd1–Pd2–Pd3–Ag2 is 89.5°, very close to the value in the Ni–Ag structure.

The average intramolecular H-bonding distance (2.41 (3) Å) is shorter than the 2.626 Å reported for $Pd(HDMG)_2$,[15b,16a] but it is longer than that (2.35 (3) Å) in the Ni–Ag structure. However, this is not unexpected because the H-bonding distance in $M(HDMG)_2$ complexes[26,27] is directly proportional to the size of the metal ion. Other bond distances and angles are summarized in Tables III and IV.

$[Ni(\delta\text{-HCQD})_2Ag]_3 \cdot 2.5CHCl_3$, Ni–Ag, and $[Pd(\delta\text{-HCQD})_2Ag]_3 \cdot 2CHCl_3$, Pd–Ag. Both the Ni–Ag and the Pd–Ag complexes can be prepared by adding aqueous $AgNO_3$ to a $CHCl_3$/MeOH solution of the corresponding $M(\delta\text{-HCQD})_2$ complex according to

$$3M(\delta\text{-HCQD})_2 + 3Ag^+ \xrightarrow[\text{MeOH/CHCl}_3]{H_2O} [M(\delta\text{-HCQD})_2Ag]_3 + 3H^+ \quad (1)$$

$$M = Ni^{2+} \text{ or } Pd^{2+}$$

The ^{13}C NMR spectrum of the Ni–Ag complex in $CDCl_3$ solvent exhibits twelve peaks for the C atoms. On the basis of assignments made in the ^{13}C NMR spectrum of $Ni(\delta\text{-HCQD})_2$,[3] the four peaks at 153.76, 153.49, 147.42, and 147.31 ppm downfield from Me_4Si may be assigned to those of the oxime C atoms. The solid-state structure suggests, however, that only two oxime ^{13}C resonances should be observed. Since the ^{107}Ag and ^{109}Ag isotopes have a spin of $^1/_2$, spin–spin coupling between C and Ag may occur. However, this possibility may be dismissed because only two peaks at 153.70 and 142.49 ppm are observed for the oxime C atoms in the similar Pd–Ag complex. It therefore appears that Ni–Ag either has a different structure or is a mixture of structures in solution.

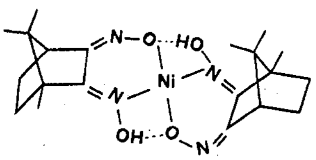

Figure 5. Structure of $Ni(\alpha\text{-HCQD})_2$.

The IR spectrum of the Ni–Ag complex in a KBr pellet no longer shows an absorption band at 1690 cm^{-1} corresponding to the oxygen-coordinated oxime $\nu(C{=}N)$ vibration found in $Ni(\delta\text{-HCQD})_2$.[2,3] Instead, a new band is observed at 1615 cm^{-1}, which is most likely the $\nu(C{=}N)$ frequency of the oxime group coordinated to both the Ag and Ni ions. The other $\nu(C{=}N)$ absorption, which probably arises from the oxime which is N-coordinated to Ni, remains unchanged at 1560 cm^{-1}, as previously reported for $Ni(\delta\text{-HCQD})_2$.[2] The bands at 1605 and 1550 cm^{-1} in the IR spectrum of the Pd–Ag complex in a KBr pellet are very similar to those of Ni–Ag.

$[Ni(\alpha\text{-HCQD})_2Ag] \cdot 0.5AgNO_3 \cdot H_2O$ and $[Pd(\alpha\text{-HCQD})_2Ag] \cdot 0.5AgNO_3$. Both complexes can be prepared by adding aqueous $AgNO_3$ to a MeOH/$CHCl_3$ solution of the corresponding $M(\alpha\text{-HCQD})_2$ complex. The difference between the starting material $M(\alpha\text{-HCQD})_2$ and $M(\delta\text{-HCQD})_2$, mentioned in an earlier section, is the isomeric form of the $HCQD^-$ ligand. In $Ni(\alpha\text{-HCQD})_2$, the oxime N atom coordinated to the metal ion is closer to the bridgehead methyl group, as shown in Figure 5 (compare Figure 1). The reaction of $M(\alpha\text{-HCQD})_2$ with $AgNO_3$ proceeds in a manner very similar to that of $M(\delta\text{-HCQD})_2$ (eq 1).

In contrast to the Ni–Ag and Pd–Ag complexes, both of the products $[Ni(\alpha\text{-HCQD})_2Ag] \cdot 0.5AgNO_3 \cdot H_2O$ and $[Pd(\alpha\text{-HCQD})_2Ag] \cdot 0.5AgNO_3$ obtained from the reaction of $M(\alpha\text{-HCQD})_2$ with $AgNO_3$ are not soluble in common organic solvents such as alcohols, $CHCl_3$, CH_3CN, and Me_2SO. This low solubility may be the result of the cocrystallization of a hexanuclear metal cluster similar to those of Ni–Ag or Pd–Ag with $AgNO_3$. However, there is no evidence to exclude a structure $Ag_3[M(\alpha\text{-HCQD})_2]_2NO_3$ in which only two $M(\alpha\text{-HCQD})_2^-$ units coordinate to the chain of three Ag atoms. The IR spectrum of $[Ni(\alpha\text{-HCQD})_2Ag] \cdot 0.5AgNO_3$ in a KBr pellet shows absorption bands at 1615 and 1550 cm^{-1} while that of $[Pd(\alpha\text{-HCQD})_2Ag].0.5AgNO_3$ exhibits absorptions at 1600 and 1550 cm^{-1}. These $\nu(C{=}N)$ vibrational frequencies, also observed in the Ni–Ag and Pd–Ag clusters, may indicate that oxime-bridged metal clusters are indeed present in these compounds as well. Compounds of the type $[Ni(\alpha\text{-HCQD})_2Ag]_3$ without $AgNO_3$ have not been isolated.

$[Ni(\delta\text{-HCQD})_2(py)_2] \cdot CHCl_3$. In a further attempt to understand the coordination chemistry of $Ni(\delta\text{-HCQD})_2$, pyridine was added to a H_2O/MeOH/$CHCl_3$ solution of $Ni(\delta\text{-HCQD})_2$, and a green paramagnetic complex, $[Ni(\delta\text{-HCQD})_2(py)_2] \cdot CHCl_3$, was isolated. The molar conductivity of the complex in CH_3CN shows that it is nonionic, which suggests that a bis(pyridine) adduct of $Ni(\delta\text{-HCQD})_2$ is formed. Its infrared spectrum taken in a KBr pellet shows $\nu(C{=}N)$ absorptions at 1610 and 1550 cm^{-1}. These are indeed very similar to those (1615 and 1560 cm^{-1}) observed in the Ni–Ag complex. Although it is unlikely that a hexanuclear metal cluster is formed, it may suggest that the *trans*-N_2O_2 coordination around Ni(II) has changed to *cis*-N_2O_2.

In an effort to determine if $[Ni(\delta\text{-HCQD})_2(py)_2] \cdot CHCl_3$ is simply a 2:1 adduct of pyridine with *trans*-N_2O_2 $Ni(\delta\text{-HCQD})_2$, the UV–visible spectrum of $Ni(\delta\text{-HCQD})_2$ in $CHCl_3$ was studied in the presence and absence of pyridine. In fact, there is no reaction of $Ni(\delta\text{-HCQD})_2$ with pyridine since its

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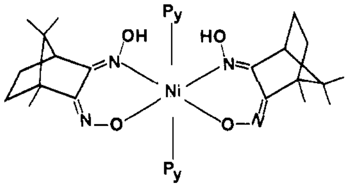

Figure 6. Proposed structure of [Ni(δ-HCQD)$_2$(py)$_2$]·CHCl$_3$.

absorption at 576 nm remains unchanged over a period of several days. Also there is no evidence of the 614-nm absorption characteristic of Ni(δ-HCQD)$_2$(py)$_2$. Moreover, the pyridine solution remains diamagnetic, which suggests that the Ni(δ-HCQD)$_2$ retains its square-planar geometry even in the presence of excess pyridine. These observations strongly indicate that Ni(δ-HCQD)$_2$(py)$_2$ is not a simple trans adduct of Ni(δ-HCQD)$_2$, Figure 1. A possible structure for this complex is the one shown in Figure 6 in which the (HCQD$^-$)$_2$ coordination around the Ni is now *cis*-N$_2$O$_2$ as suggested by the IR results. Further evidence in support of this structure is the fact that addition of AgNO$_3$ to a H$_2$O/MeOH/CHCl$_3$ solution of [Ni(δ-HCQD)$_2$(py)$_2$]·CHCl$_3$ readily yields the Ni–Ag cluster.

The solvent (H$_2$O/MeOH/CHCl$_3$) plays an important role in the preparation of Ni(δ-HCQD)$_2$(py)$_2$. Perhaps its high polarity promotes the isomerization of *trans*-N$_2$O$_2$ Ni(δ-HCQD)$_2$ to the *cis*-N$_2$O$_2$ isomer which then reacts with pyridine.

Since our attempts to prepare similar Ni–Ag cluster complexes with Ni(HDMG)$_2$ and Pd(β-HCQD)$_2$ (in the ternary solvent system) failed, it becomes evident that N,O-chelation of the ligand to the metal is probably a necessary condition for the formation of these hexanuclear cluster complexes.

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Registry No. Ni–Ag, 74744-20-0; Pd–Ag, 74744-21-1; Ni(δ-HCQD)$_2$(py)$_2$, 74511-62-9; Ni(α-HCQD)$_2$Ag, 74498-59-2; Pd(α-HCQD)$_2$Ag, 74511-63-0; Ni(δ-HCQD)$_2$, 52139-64-7; Pd(δ-HCQD)$_2$, 72100-35-7; Ni(α-HCQD)$_2$, 52231-70-6; Pd(PhCN)$_2$Cl$_2$, 14220-64-5.

Supplementary Material Available: Tables of observed and calculated structure factors for [Ni(δ-HCQD)$_2$Ag]$_3$·2.5CHCl$_3$ and for [Pd(δ-HCQD)$_2$Ag]$_3$·2CHCl$_3$ and complete tables of interatomic distances and angles and least-squares planes (36 pages). Ordering information is given on any current masthead page.

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Protonation of Dimethylmercury. Complexing Reactions of CH_3Hg^+ in the Gas Phase

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The reactions of dimethylmercury have been examined in a high-pressure, field-free, chemical ionization source with methane as the reagent gas. Both CH_3Hg^+ and $(CH_3)_2HgH^+$ are formed by protonation of $(CH_3)_2Hg$, and both react with $(CH_3)_2Hg$ to yield $(CH_3)_3Hg_2^+$ as the final stable product. This ion reacts with added aromatic, olefinic, and n-donor bases to yield stable methylmercury adduct ions, CH_3HgB^+. The order of stability of these complexes parallels that of the protonated analogues BH^+. It is suggested that $(CH_3)_3Hg_2^+$ and $(CH_3)_2HgH^+$ have similar structures which arise from the attack of the electrophilic CH_3Hg^+ or H^+ on the CH_3Hg–CH_3 σ bond.

The cleavage of transition metal–carbon σ bonds by electrophilic reagents has elicited considerable attention of late.[1] We have been particularly interested in the cleavage reactions of compounds of the type η^5-$C_5H_5Fe(CO)_2R$ with the halogens,[2] mercury(II),[3] and copper(II)[4] and have very recently investigated the stereochemistry of the acid (DCl, CF_3CO_2D) cleavage of the compounds *cis-* and *trans-*(4-methylcyclohexyl)$Fe(CO)_2(\eta^5$-$C_5H_5)$.[5] Cleavage in the latter cases yields the corresponding monodeuterated hydrocarbons, with retention of configuration, via a mechanism believed to involve direct protonation of a nonbonding metal d orbital, the highest occupied molecular orbital (HOMO).

During the course of the acid-cleavage work, there appeared a report on the gas-phase protonation of $CH_3Mn(CO)_5$, studied with the use of ICR spectrometry.[6] Interestingly, the ICR data were interpreted in terms of protonation of the manganese compound at *two* sites, either the essentially d orbitals of e and b_2 symmetry or the combination of an e orbital and the a_1 Mn–C σ-bonding orbital. It was possible to correlate the proton affinities of the two sites with photoelectron data for the compound, thus demonstrating the possibility of valuable correlations between the solution-phase and gas-phase protonation reactions of volatile organo transition-metal compounds and their gas-phase ionization potentials.

We have therefore initiated a study of the gas-phase chemistry of representative organometallic compounds, utilizing high-pressure mass spectrometry. We report here a chemical ionization study of dimethylmercury, $(CH_3)_2Hg$, surprisingly little studied heretofore in spite of its ready availability and high volatility. We also report preliminary results on the formation of complex ions by the electrophilic reactions of the methylmercury cation, CH_3Hg^+, with a series of donor ligands.

Experimental Section

A high-pressure, electron-impact ion source patterned on the one described by Kebarle[7] was built. It was usually operated in the field-free mode at ambient temperature, but a repeller field was available. Most results were obtained in the continuous-ionization mode, but time-resolved studies could be made with a pulsed electron beam.[7] The 2-kV beam was pulsed on for 58 μs, and the decay of

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