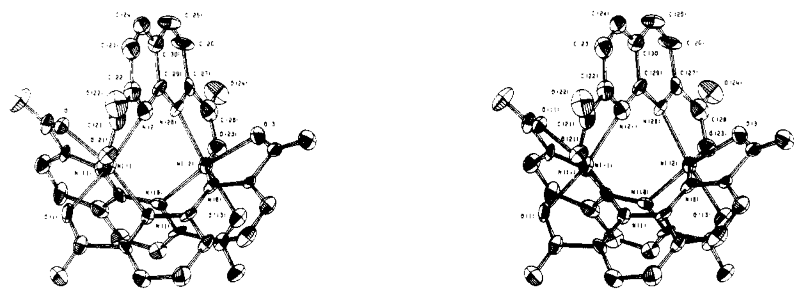

Figure 1. ORTEP stereoview of the tris(1,8-naphthyridine-2,7-dicarboxylato)dinickelate(II) anion showing the atomic numbering and thermal ellipsoids.

Table III. Distances (Å) and Angles (deg)[a] in the $Ni(H_2O)_6^{2+}$ Ion

Ni(3)–O(W1)	2.091 (10)	Ni(3)–O(W2)	2.071 (10)
Ni(3)–O(W2)	2.059 (11)	Ni(3)–O(W4)	2.061 (10)
Ni(3)–O(W3)	2.062 (12)	Ni(3)–O(W6)	2.022 (1)
O(W1)–Ni(3)–O(W2)	92.8[a]	O(W2)–Ni(3)–O(W6)	177.7
O(W1)–Ni(3)–O(W3)	93.0	O(W3)–Ni(3)–O(W4)	177.1
O(W1)–Ni(3)–O(W4)	89.6	O(W3)–Ni(3)–O(W5)	88.1
O(W1)–Ni(3)–O(W5)	178.5	O(W3)–Ni(3)–O(W6)	90.0
O(W1)–Ni(3)–O(W6)	89.2	O(W4)–Ni(3)–O(W5)	89.4
O(W2)–Ni(3)–O(W3)	90.9	O(W4)–Ni(3)–O(W6)	88.6
O(W2)–Ni(3)–O(W4)	90.4	O(W5)–Ni(3)–O(W6)	91.9
O(W2)–Ni(3)–O(W5)	86.1		

[a] All angles ±0.4°.

Table IV. Summary of Metal–Ligand Distances (Å), Deviations (Å) from the Ligand Plane (DEV), Angles (deg) between the Planes of the Napy Rings (BEND), Angles (deg) between the Carboxy Plane and the Napy Ring (ANGLE), and Displacement (Å) of the Ni Atoms from the Plane of the Carboxy Group (DEV1 or DEV2) in the $Ni_2(2,7\text{-dc-}1,8\text{-napy})_3^{2-}$ Ion

	n		
ligand	0	1	2
Ni(1)–N(*n*1)	2.130 (9)	2.092 (10)	2.135 (11)
Ni(2)–N(*n*8)	2.133 (9)	2.131 (9)	2.080 (9)
Ni(1)–O(*n*1)	2.062 (9)	2.058 (8)	2.049 (8)
Ni(2)–O(*n*3)	2.054 (9)	2.050 (8)	2.027 (9)
DEV(Ni(1))	–0.847	0.886	1.210
DEV(Ni(2))	0.992	–1.019	–0.674
BEND	6.9 (4)	6.1 (4)	5.1 (4)
ANGLE-1	14.0 (9)	21.3 (5)	22.2 (4)
ANGLE-2	14.6 (8)	15.9 (4)	10.0 (7)
DEV1(Ni(1))	0.080	–0.135	0.146
DEV2(Ni(2))	0.234	0.271	0.184

of lattice and/or coordinated water. Consequently, a crystal structure determination was undertaken to elucidate the mode of bonding of the nickel ion with our unusual multidentate ligand. The structural study indicated that the compound was $Ni(H_2O)_6^{2+}Ni_2L_3^{2-}\cdot 5H_2O$.

The crystals consist of $Ni(H_2O)_6^{2+}Ni_2L_3^{2-}$ ions in a hydrogen-bonded network involving the five water molecules. The cation is shown in the supplementary material and a stereoview of the anion in Figure 1. The Ni(3)–OH_2 distances in the cation range from 2.022 (11) to 2.091 (10) Å, with an average of 2.061 (22) Å. An examination of the various possible hydrogen bonds involving O(W1) and O(W6) does not provide any clue as to why two of the Ni–O distances differ from the mean.

The anion is rather unusual. Although M_2L_3 systems have been proposed,[12] we believe that the present structure is the first confirmed example of this stoichiometry in a metal complex. A number of features of the anion were surprising and are summarized in Table IV. The Ni–O distances range from 2.027 to 2.062 Å, with an average of 2.050 (12) Å, slightly shorter than in the cation. The shortening of Ni–O is not surprising since we have neutral H_2O vs. the charged carboxy group. The Ni–N distances range from 2.080 to 2.135 Å, with an average of 2.117 (24) Å, slightly longer than Ni–O, as expected. However, the Ni atoms all showed large displacements from the plane of the coordinating six-membered nitrogen ring, ranging from 0.674 to 1.210 Å. These displacements of the Ni atoms from the ring appear to be by far the largest observed in metal–naphthyridine ligand complexes. Similarly, the angle between the two planes in the naphthyridine ring system (6.9, 6.1, and 5.1°) are the largest that have been observed in the normally planar fused ring system. An analysis of the deviations from the various planes suggests a distortion to increase the distance between the two coordinating nitrogen atoms. The deviations of a Ni atom from the plane of the carboxy group is much less (0.080–0.271 Å), but the carboxy groups are twisted relative to the corresponding ring plane. The overall picture is one of large adjustments by both metal ions and naphthyridine ligands from the usual coordination geometry in order to form the $Ni_2L_3^{2-}$ ion. The geometry of the 2,7-dc-1,8-napy ligand prevents a small transition-metal ion from coordinating to all four donors in a monomer with a 1:1 ratio. Furthermore, three of the coordinating sites around a metal in a binuclear complex are blocked, further restricting the available options. Further studies with mono- and disubstituted 1,8-napy ligands are in progress to extend these observations.

Acknowledgment. We thank the Center for Instructional Research Computing Activities, University of Florida, for a grant of computer time.

Registry No. $Ni(H_2O)_6^{2+}Ni_2L_3^{2-}\cdot 5H_2O$, 98735-40-1.

Supplementary Material Available: A view of the $Ni(H_2O)_6^{2+}$ cation and tables of thermal parameters, atomic coordinates for the hydrogen atoms, bond distances, bond angles, and observed and calculated structure amplitudes (26 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic Characterization of Substitution-Inert Cobalt(III) Complex Bonded Silicas

C. Allen Chang,*[†] Chen-Shi Huang,[†] and Paul D. Murphy[‡]

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The preparation of silica surface-confined materials has been of recent interest for a variety of applications such as chemical analysis and separation, energy conversion, and catalysis.[1-4] In chromatography, various surface-modified silicas have been prepared and characterized. For example, optically active amino acids have been immobilized for ligand-exchange chromatography of dansyl-DL-amino acids.[5] Bonded silica phases using silanes

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with octadecyl, aromatic, amino, diamine, and cyano groups have also been studied by various spectroscopic techniques, e.g., nuclear magnetic resonance,[3,6-9] infrared,[6,10,11] fluorescence,[12] and electron spin resonance,[13] photoacoustic spectroscopy,[6,14-16] X-ray fluorescence,[17] and ESCA.[18] Information concerning the surface coverage of the bonded groups, the conformations of the bonded groups, the surface Si–OH quantitation, dynamics, site–site interactions, surface local environment, etc. can now be obtained. These are obviously extremely important for the understanding of surface activities and mechanisms.

We have been interested in the use of substitution-inert cobalt(III) complexes in liquid chromatography. One application is to use these metal complex bonded phases for normal phase separations. As a result of our efforts in this area, we have reported the separation of isomers of dihydroxybenzene,[19] carbohydrates,[20] substituted anilines,[21] and some organometallic compounds,[22] as compared with the use of other columns. Unique selectivities are observed in many separations, presumably due to the three-dimensional structures of these metal complexes and the ion-dipole and hydrogen-bonding interactions. In order to assess the retention contribution of these new surface-derivatized materials, we have carried out additional characterizations. In this paper, we wish to report our characterizations of such materials using solid-state NMR and diffuse-reflectance spectroscopic methods and other techniques. It should be noted that Chow and Grushka had described the preparation of one of the cobalt(III) complex bonded silicas, i.e. tris(ethylenediamine)cobalt(III) chloride, $[Co(en)_3]Cl_3$–silica, for the separation of nucleosides and nucleotides; however, detailed characterization was not reported.[23]

Experimental Section

Reagents. Partisil-10 solid silica support was obtained from Whatman (Clifton, NJ). The surface area is 396 m^2/g with surface silanol groups 8.0 ± 0.5 $\mu mol/m^2$. [3-[(2-Aminoethyl)amino]propyl]trimethoxysilane was purchased from Silar Laboratories (Scotia, NY). All other compounds and reagents were of reagent grade and were obtained from various sources.

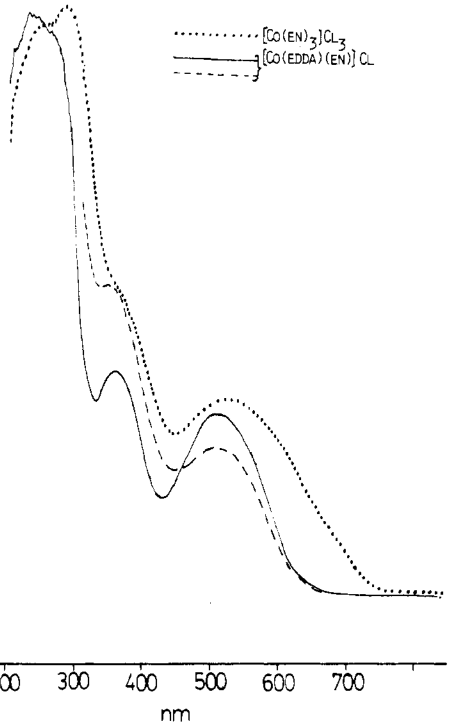

Figure 1. Diffuse-reflectance spectra of $[Co(en)_3]Cl_3$ and $[Co(edda)(en)]Cl$ bonded silicas.

Diffuse-Reflectance Optical Measurements. Diffuse-reflectance spectra were measured on a Perkin-Elmer Model 330 UV–vis–near-IR spectrometer with a Hitachi integration sphere reflectance attachment. All samples were prepared as lightly packed powders pressed between optical grade quality plates. A freshly prepared $BaSO_4$ surface provided the reference signal. Reflectance data are reported in absorbance scale rather than percent reflectance scale in order to make them similar to conventional absorbance spectra. Slit widths were fixed at 3 nm, and 50 nm/min scan speed and 4 s time constant were used.

Carbon-13 Solid-State NMR Measurements. The solid-state ^{13}C NMR spectra were recorded with an IBM Instruments, Inc., 200-MHz solids accessory (NR 200) and a Bruker Instruments, Inc., WP200SY console. ^{13}C resonance was at 50.33 MHz. Spectra were recorded with cross polarization and magic angle spinning between 4.5 and 5 kHz. Spectral parameters: $T_{cp} = 2$ ms, $T_{rep} = 3$ s, SW = 20 kHz, FW = 25 kHz, HH = 50 kHz.

X-ray Fluorescence (XRF) Measurements. The procedure for the XRF determination of silica surface-confined monolayer cobalt was published previously.[17]

Results and Discussion

$[Co(en)_3]Cl_3$ Bonded Phases. Our general procedure to derivatize substitution-inert metal complexes on silica surfaces was published previously.[24] Diamine bonded silicas were prepared by reacting dry silicas with [3-[(2-aminoethyl)amino]propyl]trimethoxysilane in dry toluene. The diamine bonded silicas were then reacted with the *cis*-dichlorocobalt(III) complex of appropriate ligand(s) in aqueous solutions. Thus, *cis*-[dichlorobis(ethylenediamine)]cobalt(III) chloride, $[Co(en)_2Cl_2]Cl$, was used for the final coupling step to prepare the tris(ethylenediamine)cobalt(III) chloride, $[Co(en)_3]Cl_3$, bonded phase. However, in the first report by Chow and Grushka[23] and later in our work, the color of the product was reddish instead of yellow. The diffuse-reflectance spectrum of this red material is shown in Figure 1. A broad peak with a maximum at 524 nm and a shoulder at 360 nm are observed. The broad peak at 524 nm may indicate a mixture of unreacted adsorbed $[Co(en)_2(H_2O)_2]Cl_3$ (λ_{max} 534 nm), which is the hydrolysis product of $[Co(en)_2Cl_2]Cl$ and has a ligand field N_4O_2, and the complex with which the chelate ring of the coupling diamine did not close during the reaction. The latter has a ligand field of N_5O (λ_{max} ~490 nm).

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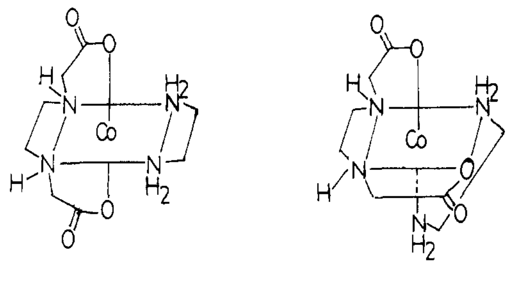
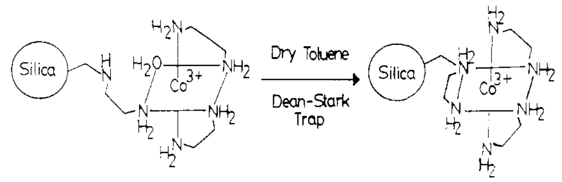


Symmetrical-cis

Unsymmetrical-cis

Figure 2. Two isomers of the $[Co(edda)(en)_2]^+$ complex.

To complete the derivatization, we have introduced one more reaction step simply by refluxing the red material in dry toluene with a Dean–Stark trap[25] (eq 1). The final product was indeed

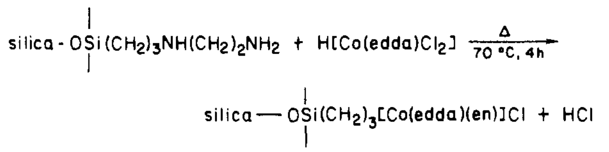


(1)

yellow. The diffuse-reflectance spectrum shows a maximum at 460 nm, consistent with a N_6 ligand field.

It should be noted that the last added experimental step not only converts the ligand field from N_5O to N_6 but also increases slightly the surface coverage of the substitution-inert metal complex from 0.9 to 1.0 $\mu mol/m^2$, as confirmed by an X-ray fluorescence determination of surface monolayer cobalt.[17] Presumably, quite a few loosely bonded complexes were present before the final refluxing step, which could either be washed away or be anchored more tightly on the surface. The last reflux does just the latter. The material should be stored in a dry environment. In a humid place, apparently a surface-catalyzed reverse reaction of eq 1 can occur.

[Co(edda)(en)]Cl Bonded Phase. The preparation of (ethylenediamine)(ethylenediamine-*N,N′*-diacetato)cobalt(III) chloride, $[Co(edda)(en)]Cl$, bonded phases is similar to that of the $[Co(en)_3]Cl_3$ bonded phases (eq 2). $H[Co(edda)Cl_2]$ was prepared



$$\text{silica-OSi(CH}_2)_3\text{NH(CH}_2)_2\text{NH}_2 + \text{H[Co(edda)Cl}_2] \xrightarrow[70\ ^\circ\text{C, 4h}]{\Delta} \text{silica—OSi(CH}_2)_3\text{[Co(edda)(en)]Cl} + \text{HCl} \quad (2)$$

similarly to a published method.[26] The final product is red. Two diffuse-reflectance spectra for materials from separate preparations using silicas from different batches are shown in Figure 1. It is observed that two maxima are apparent at 505 and 360 nm, consistent with a N_4O_2 ligand field. However, it is not certain which isomer has resulted on the surface because two isomers are possible (Figure 2).

The s-cis isomer is the dominant product under normal synthetic conditions.[27] It has its lowest energy absorption band centered at 530 nm.[26,27] A shoulder at 450 nm is also observed. On the other hand, the less abundant uns-cis isomer has its lowest energy absorption band centered at 500 nm. Since the resolution of diffuse-reflectance measurements was not good enough, it is not clear whether a shoulder is present at 450 nm for the metal complex bonded silica. If surface-induced shift of the maximum is not considered, the final product would be more likely the uns-cis isomer, which may be produced by a surface catalytic process because the starting reagent was *s-cis*-$H[Co(edda)Cl_2]$. The detailed mechanism of this isomerization is not clearly understood.

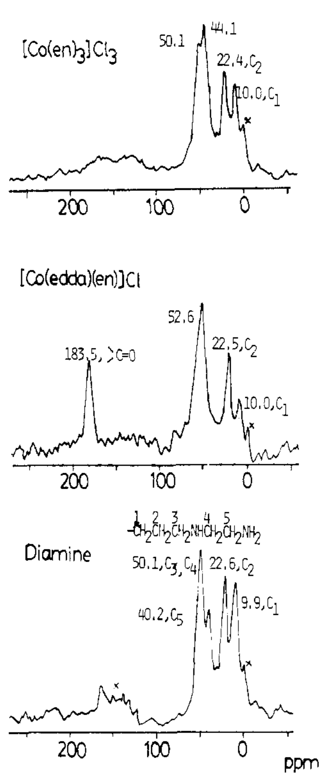


Figure 3. Solid-state CP-MAS ^{13}C NMR spectra of the diamine, $[Co(edda)(en)]Cl$, and $[Co(en)_3]Cl_3$ bonded silicas.

Solid-State Carbon-13 NMR Spectra. The solid-state cross polarization and magic angle spinning (CP-MAS) ^{13}C NMR spectra of the diamine, $[Co(edda)(en)]Cl$, and $[Co(en)_3]Cl_3$ bonded silicas are shown in Figure 3.

The assignments of spectral peaks for the diamine bonded silicas were made by comparison with those done in a polar slurry.[28,29] For example, it is observed that the diamine bonded silica in a D_2O suspension shows five ^{13}C chemical shifts at 11.7, 23.0, 40.4, 51.0, and 52.0 ppm, consistent with the present observation. As far as the Co(III) complex bonded silicas are concerned, peak assignment was more difficult for methylene carbons with chemical shifts greater than 30 ppm. This is not only because there is relatively poor resolution for solid-state NMR as compared to slurry and solution NMR but also because the substitution-inert metal complex bonded silicas have mixed surface coverage of both complex and residual diamine.[24]

The carbonyl chemical shift of $[Co(edda)(en)]Cl$ bonded silica, i.e. 183.5 ppm, is consistent with those observed for model complexes in D_2O solution, i.e. a single peak at 186.68 ppm for the s-cis isomer and two close peaks centered at 183.35 ppm for the uns-cis isomer.[30] However, care must be exercised in correlating solid-state NMR chemical shifts with those observed in solution because, at least in two cases, the solid-state spectra show significant high-field shift, i.e. 6 ppm, for the CO carbons of $LRu(CO)_4$ bonded silicas where L is a phosphine ligand.[3]

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Registry No. $[Co(en)_2Cl_2]Cl$, 14040-32-5; $H[Co(edda)Cl_2]$, 53152-23-1.

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