tensity. The magnitude of $^1J(^{195}\text{Pt},^{31}\text{P})$ in complexes of PCy_3 is known to follow the predicted trends due to trans-influence changes in supporting ligands in a systematic manner,[1] and an increase of ca 200 Hz on isomerization would be anticipated. The ^1H NMR spectrum similarly shows a decrease in intensity of the broadened resonance at 3.20 ppm and a new, sharp resonance, with a peak width at half-height of ca 1.1 Hz, at 3.63 ppm with $^3J(^{195}\text{Pt},^1\text{H}) = 22$ Hz. This confirms that the sulfoxide remains bonded via sulfur and is further evidence for the cis geometry of the complex since the decrease in $^4J(^{31}\text{P},^1\text{H})$ upon isomerization (i.e. $^4J(^{31}\text{P},^1\text{H})_{cis} \ll {}^4J(^{31}\text{P},^1\text{H})_{trans}$) leads to line narrowing. After 8 months at room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicates that isomerization is ca. 85% complete (by peak heights) and the IR spectrum of the isolated product shows $\nu(\text{S==O}) = 1135$ cm^{-1}, confirming S-bonding of the sulfoxide.[7] Thus, trans-$[\text{PtCl}_2(\text{PCy}_3)(\text{L})]$ complexes can undergo trans $\rightarrow$ cis isomerization, as commonly encountered for analogues with less sterically demanding tertiary-phosphine ligands, but at an astonishingly slow rate under ambient conditions. With the PPh_3 analogue, for example, the isomerzation must be extremely rapid as we have been unable to isolate trans-$[\text{PtCl}_2(\text{PPh}_3)(\text{Me}_2\text{SO})]$ by any method so far attempted, and indeed, addition of Me_2SO to a CDCl_3 solution of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPh}_3)_2]$, followed by immediate examination by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, shows only the presence of cis-$[\text{PtCl}_2(\text{PPh}_3)(\text{Me}_2\text{SO-}S)]$.

Cleavage of $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ with the larger nucleophile Bz_2SO was investigated to see if the trans $\rightarrow$ cis isomerization could be completely retarded. In fact, a new isomerization process was found to occur. Thus, reaction of $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ with 2 equiv of Bz_2SO in refluxing CH_2Cl_2 for 20 h, followed by precipitation with hexane and examination of the solid produced by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy in CDCl_3 solution, shows the presence of unreacted dimer and a new species with $\delta = 19.64$ and $^1J(^{195}\text{Pt},^{31}\text{P}) = 3206$ Hz. The value of $^1J(^{195}\text{Pt},^{31}\text{P})$ differs considerably from the value for the PCy_3 trans to Cl arrangement in cis-$[\text{PtCl}_2(\text{PCy}_3)(\text{Me}_2\text{SO})]$ (3378 Hz) and implies formation of a trans cleavage product. The ^1H NMR spectrum, however, shows *no* deshielded resonances with coupling to ^{195}Pt for the diastereotopic benzylic protons of a S-bonded sulfoxide. Instead, a single peak at 3.89 ppm, with no coupling to ^{195}Pt, is observed. This peak position coincides with the resonance position for the benzylic protons of free Bz_2SO. Coordination of Bz_2SO to platinum via oxygen would be consistent with these data. Thus, O-bonding leads to very small or negligible deshielding of the α-protons of sulfoxides[7] and coupling of these protons to the metal center is not observed.[7] The value of $^1J(^{195}\text{Pt},^{31}\text{P})$ is also consistent with a trans arrangement of PCy_3 and $\text{Bz}_2\text{SO-}O$ ligands, although comparative data for platinum(II) phosphine complexes with oxygen-donor ligands are scarce. O-Bonding of sulfoxides to platinum(II) is observed in sterically congested systems[7] and may be promoted by tertiary-phosphine ligands with large cone angles.[9] The initial product of the cleavage of $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PCy}_3)_2]$ by Bz_2SO is thus formulated as trans-$[\text{PtCl}_2(\text{PCy}_3)(\text{Bz}_2\text{SO-}O)]$.

Upon standing in CDCl_3 solution, the complex undergoes a slow isomerization. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, peaks associated with trans-$[\text{PtCl}_2(\text{PCy}_3)(\text{Bz}_2\text{SO-}O)]$ are replaced by a resonance at 23.28 ppm with $^1J(^{195}\text{Pt},^{31}\text{P}) = 3396$ Hz. The magnitude of $^1J(^{195}\text{Pt},^{31}\text{P})$ indicates a geometry with PCy_3 trans to Cl and so implies a trans $\rightarrow$ cis isomerization. In the ^1H NMR spectrum, however, new resonances appear for the benzylic protons, which are substantially deshielded, $\delta(\text{H}_A) = 5.61$ and $\delta(\text{H}_B) = 4.41$, and exhibit coupling, $J(\text{H}_A,\text{H}_B) = 12.3$ Hz. The more shielded resonance is observably coupled to platinum, with $^3J(^{195}\text{Pt},\text{H}_B) = 31$ Hz while the less shielded proton is not. This pattern for the diastereotopic protons is typical of an S-bonded benzylic sulfoxide, as observed previously in related complexes by both ourselves[6] and others.[10] After 8 months in CDCl_3 solution, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicates that isomerization to the cis-S-bonded

isomer is ca. 90% complete (by peak heights). The IR spectrum of the isolated product shows $\nu(\text{S==O}) = 1130, 1184$ cm^{-1} as shoulders on the bands at 1119 and 1177 cm^{-1} due to the PCy_3 group, confirming S-bonding of the sulfoxide.

The reactions of Me_2SO and Bz_2SO with $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2$-$(\text{PCy}_3)_2]$ thus differ considerably. The initially formed cleavage product is the trans-$[\text{PtCl}_2(\text{PCy}_3)(\text{L})]$ complex in both cases, but Me_2SO is S-bonded while Bz_2SO is O-bonded. Both complexes undergo slow isomerization to the corresponding cis-S-bonded isomers. The Bz_2SO system is exceptional since the geometric isomerization is accompanied by a change in the mode of coordination of the ambidentate sulfoxide ligand. We are not aware of any related examples of such phenomena in sulfoxide coordination chemistry, and it is clear that a fine balance of steric and electronic effects must control product formation. Thus, the initially formed cleavage product contains the sterically favored, but electronically disfavored,[11] O-bonded sulfoxide trans to the bulky PCy_3 group while the isomerization product contains the electronically favored,[11] but sterically disfavored, S-bonded sulfoxide cis to the bulky PCy_3 ligand. Systematic studies of steric and electronic effects may shed light on the factors governing such processes.[6] The detailed mechanism of the unusual isomerization process has not been investigated but, in view of the steric congestion at the metal center, a dissociative pathway may be possible.[12,13]

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Synthesis and Structure of Hexaaquanickel(II) Tris(1,8-naphthyridine-2,7-dicarboxylato)dinickelate(II) Pentahydrate

Hossein Aghabozorg, Ruth C. Palenik, and Gus J. Palenik*

The 1,8-naphthyridine (1,8-napy) ring can function as either a monodentate, bidentate, or binuclear ligand.[1] The binuclear mode is particularly interesting since the two metal ions are in close proximity and metal–metal interactions can occur.[2–4] However, in the majority of the 1,8-napy complexes the ligand

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Table I. X-ray Diffraction Data

(A) Crystal Data

formula: $C_{30}H_{34}N_6O_{23}Ni_3$

cryst system: monoclinic	space group: $P2_1/c$
$a = 13.263$ (4) Å	$\alpha = 90.0°$
$b = 16.303$ (6) Å	$\beta = 94.68$ (2)°
$c = 17.540$ (5) Å	$\gamma = 90.0°$
vol = 3780 (2) Å	$Z = 4$
$D_m = 1.80$ g cm^{-3}	$D_c = 1.797$ g cm^{-3}
cryst size = 0.27 × 0.09 × 0.03 mm	$\mu = 15.8$ cm^{-1}

(B) Solution and Refinement

no. of reflcns measd: 4979 (Mo Kα; graphite monochromator)

no. of reflcns used: 2876 ($I \geqslant 2.00(I)$)

no. of variables: 559 ($w = 1/\sigma^2(F_o)$)

$R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.063$; R(weighted) $= 0.067$

GOF = 0.82

functions in either a monodentate or bidentate manner. Our approach, as well as others recently,[5-8] has been to add functional groups in the 2,7-positions of 1,8-napy to increase the probability of forming binuclear complexes. However, one of the major obstacles in synthesizing 1,8-napy ligands is the low yields obtained in the preparation of starting materials.[9] As the first step in synthesizing multidentate 1,8-napy ligands, we have developed an improved synthesis of 2,7-dimethyl-1,8-naphthyridine (2,7-dm-1,8-napy) and 2,7-dicarboxy-1,8-naphthyridine (2,7-dc-1,8-napy).[10] The reaction of nickel nitrate with 2,7-dc-1,8-napy gave green crystals of a complex whose analysis was NiL·3.5H$_2$O, where L is the dianion of 2,7-dc-1,8-napy. However, the X-ray structure demonstrated that the complex was Ni(H$_2$O)$_6^{2+}$Ni$_2$L$_3^{2-}$·5H$_2$O.[11]

Experimental Section

Materials. The synthesis of 1,8-naphthyridine-2,7-dicarboxylic acid has been reported.[8] Our preparation of 2,7-dm-1,8-napy and the conversion to 2,7-dc-1,8-napy will be reported elsewhere.[10] All other solvents and chemicals were reagent grade.

Preparation of Hexaaquanickel(II) Tris(1,8-naphthyridine-2,7-dicarboxylato)dinickelate(II) Pentahydrate. Lithium hydroxide (0.084 g, 2 mmol) and 2,7-dc-1,8-napy (0.436 g, 2 mmol) were heated in methanol. Nickel nitrate hexahydrate (0.582 g, 2 mmol) was added, and the green slurry was heated for about 1 h. The slurry was stirred at room temperature overnight and then filtered. The residue was heated in 50 mL of water to give a clear solution, which was filtered and left at room temperature. The next day green bars suitable for X-ray diffraction studies were obtained. Anal. Calcd for C$_{30}$H$_{34}$N$_6$O$_{23}$Ni$_3$ [Ni(H$_2$O)$_6^{2+}$-Ni$_2$L$_3^{2-}$·5H$_2$O]: C, 35.23; H, 3.35; N, 8.22. Found: C, 35.03; H, 3.32; N, 8.23.

The following IR bands (cm^{-1}) were observed in a Nujol mull: 1650 (ms, sh), 1645 (ms, sh), 1635 (s), 1625 (s), 1595 (ms), 1545 (m), 1440 (w), 1300 (ms), 1215 (w), 1175 (m), 1125 (m), 1115 (m), 850 (ms), 835 (w, sh), 805 (wm), 770 (m), 645 (m, br).

X-ray Structure Determination. The intensity data were measured by using a P$\bar{1}$ diffractometer with graphite-monochromatized Mo Kα radiation to a 2θ limit of 45°. A variable speed (1–24°/min) scan technique was used. The nickel atom positions were found with MULTAN; the remaining non-hydrogen atoms were located in successive Fourier syntheses. The structure was refined by full-matrix least-squares, using isotropic thermal parameters. Further refinement using anisotropic thermal parameters for all the non-hydrogen atoms was carried out by using the block approximation. The hydrogen atoms were located in a difference Fourier synthesis. The hydrogen atom contributions were included in the subsequent calculations, but their position and thermal parameters were not refined. The programs used were written or mod-

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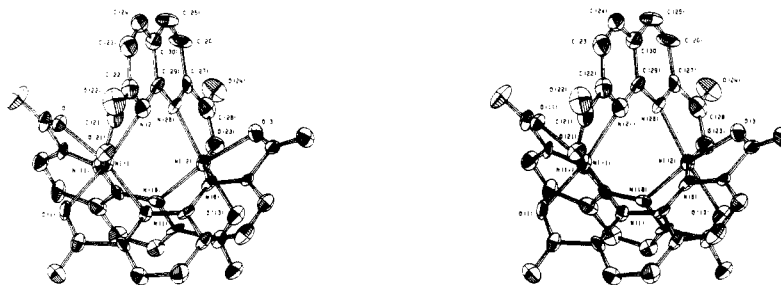(11) Aghabozorg, H.; Palenik, R. C.; Palenik, G. J. 36th SERM-ACS, Raleigh, NC, Oct 24–26, 1984; paper 310.

Table II. Final Positional Parameters (×10^4) in [Ni(H$_2$O)$_6^{2+}$][Ni$_2$(2,7-dc-1,8-napy)$_3^{2-}$]·5H$_2$O

atom	x	y	z
Ni(1)	3269 (1)	7238 (1)	5582 (1)
Ni(2)	522 (1)	7452 (1)	5096 (1)
Ni(3)	6942 (1)	7311 (1)	7128 (1)
O(W1)	6105 (7)	8224 (6)	6526 (6)
O(W2)	5854 (7)	6424 (6)	6856 (5)
O(W3)	7699 (8)	6991 (6)	6193 (6)
O(W4)	6248 (8)	7612 (7)	8100 (5)
O(W5)	7733 (8)	6400 (7)	7733 (7)
O(W6)	8022 (8)	8151 (7)	7432 (6)
O(W7)	6299 (7)	6673 (6)	4946 (6)
O(W8)	2341 (8)	2194 (7)	5620 (6)
O(W9)	2346 (9)	810 (8)	1415 (7)
O(W10)	5884 (12)	5523 (9)	8189 (8)
O(W11)	4746 (12)	588 (9)	2283 (9)
O(1)	4430 (6)	7443 (5)	4892 (5)
O(2)	5150 (8)	8388 (6)	4224 (6)
O(3)	−487 (6)	7852 (5)	5843 (5)
O(4)	−939 (7)	8998 (5)	6427 (5)
O(11)	4017 (6)	6196 (5)	5975 (4)
O(12)	4222 (8)	4878 (6)	5706 (5)
O(13)	−96 (7)	8229 (5)	4266 (5)
O(14)	−299 (7)	8344 (6)	2999 (5)
O(21)	4009 (6)	7892 (5)	6455 (5)
O(22)	4162 (8)	7953 (7)	7731 (6)
O(23)	−510 (7)	6615 (5)	4677 (5)
O(24)	−1232 (8)	5431 (6)	4993 (6)
N(1)	2850 (7)	8402 (5)	5103 (5)
N(8)	1251 (7)	8538 (5)	5538 (5)
N(11)	2679 (7)	6382 (6)	4778 (5)
N(18)	1375 (7)	7122 (6)	4164 (5)
N(21)	2339 (8)	7010 (6)	6497 (6)
N(28)	882 (7)	6492 (5)	5850 (5)
C(1)	4484 (9)	8149 (8)	4628 (7)
C(2)	3648 (9)	8730 (7)	4800 (7)
C(3)	3728 (10)	9578 (7)	4663 (7)
C(4)	3026 (11)	103 (8)	4923 (9)
C(5)	1442 (11)	235 (8)	5570 (8)
C(6)	642 (11)	9859 (7)	5864 (8)
C(7)	565 (9)	9018 (7)	5801 (7)
C(8)	−394 (10)	8596 (7)	6051 (6)
C(9)	2095 (9)	8901 (7)	5308 (7)
C(10)	2194 (9)	9768 (7)	5263 (7)
C(11)	3884 (10)	5569 (7)	5549 (8)
C(12)	3250 (8)	5703 (7)	4805 (7)
C(13)	3329 (10)	5158 (8)	4194 (7)
C(14)	2776 (11)	5354 (8)	3507 (8)
C(15)	1515 (11)	6270 (8)	2796 (7)
C(16)	896 (10)	6922 (8)	2817 (7)
C(17)	830 (9)	7338 (7)	3538 (7)
C(18)	80 (8)	8028 (7)	3604 (7)
C(19)	2063 (9)	6515 (7)	4118 (6)
C(20)	2129 (11)	6048 (8)	3471 (8)
C(21)	3769 (10)	7677 (9)	7122 (7)
C(22)	2933 (10)	7075 (9)	7140 (7)
C(23)	2811 (11)	6598 (10)	7788 (8)
C(24)	2088 (11)	6023 (10)	7763 (8)
C(25)	619 (11)	5349 (8)	7023 (7)
C(26)	41 (12)	5335 (8)	6381 (9)
C(27)	128 (9)	5939 (7)	5805 (7)
C(28)	−599 (11)	5983 (8)	5108 (8)
C(29)	1552 (9)	6486 (7)	6484 (7)
C(30)	1429 (11)	5921 (8)	7108 (7)

ified by G.J.P. The crystal data and details are summarized in Table I. The final parameters for the nonhydrogen atoms are given in Table II; tables of thermal parameters, hydrogen atom coordinates, C–C, C–N, and C–O distances and angles in the ligands, and observed and calculated structure amplitudes are available as supplementary material. The metal–ligand distances and angles in the cation and anion are given in Tables III and IV.

Results and Discussion

The shift and changes in the C=O region, 1625–1620 cm^{-1}, and ring vibrations, 770–850 cm^{-1}, suggest that the nickel is coordinated to both the ring nitrogen and carboxy oxygen atoms. Furthermore, the appearance of the peak at 645 cm^{-1} is indicative

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$_2$O)$_6{}^{2+}$ 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-dc-1,8-napy)$_3{}^{2-}$ Ion

	n		
ligand	0	1	2
Ni(1)-N(n1)	2.130 (9)	2.092 (10)	2.135 (11)
Ni(2)-N(n8)	2.133 (9)	2.131 (9)	2.080 (9)
Ni(1)-O(n1)	2.062 (9)	2.058 (8)	2.049 (8)
Ni(2)-O(n3)	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$_2$O)$_6{}^{2+}$Ni$_2$L$_3{}^{2-}$·5H$_2$O.

The crystals consist of Ni(H$_2$O)$_6{}^{2+}$Ni$_2$L$_3{}^{2-}$ 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$_2$L$_3$ 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$_2$O 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$_2$L$_3{}^{2-}$ 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.

Supplementary Material Available: A view of the Ni(H$_2$O)$_6{}^{2+}$ 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

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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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