

Preparation and Structural Characterization of Nickel(II) Catecholates

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The early literature of catecholate complexes of Ni(II) is explained with regard to both high-spin octahedral and low-spin square-planar complexes. The former contain coordinated solvent, while the latter do not. The syntheses of the paramagnetic ($S = 1$; $\mu_{\text{eff}} = 2.93 \mu_{\text{B}}$ at 300 K) octahedral Ni(II) complex $\text{Na}_2[\text{trans}-(\text{H}_2\text{O})_2(\text{cat})_2\text{Ni}^{\text{II}}] \cdot 12\text{H}_2\text{O}$ (**1a**) and the diamagnetic square-planar Ni(II) complex $\text{Na}_2[(\text{cat})_2\text{Ni}^{\text{II}}] \cdot 2\text{DMF}$ (**2**) are described. The physical and chemical properties of these Ni catecholates and their X-ray crystal structures are presented. In aqueous solution at low temperature the centrosymmetric octahedral complex is formed, which has average Ni–O distances of 2.044(3) Å (catecholate) and 2.162(3) Å (water). At higher temperature or under more weakly solvating conditions the square-planar complex is formed; the complex **2** is centrosymmetric with an average Ni–O(catecholate) distance of 1.863(3) Å. The crystals of **1a** conform to space group $C2/c$, with unit cell dimensions $a = 26.0287(8)$ Å, $b = 9.0016(3)$ Å, $c = 10.6992(3)$ Å, $\beta = 101.809(1)^\circ$, $V = 2453.8(1)$ Å³, and $Z = 4$. Those of **2** conform to space group $P2_1/m$, with unit cell dimensions $a = 6.0906(5)$ Å, $b = 13.208(1)$ Å, $c = 12.826(1)$ Å, $\beta = 95.711(1)^\circ$, $V = 1026.7(1)$ Å³, and $Z = 2$.

Introduction

Catechols (1,2-dihydroxybenzenes) are ubiquitous in biological chemistry; among other functions they act as electron donors¹ or complexing agents, notably in the high-affinity iron-binding compounds of bacteria, siderophores.² Catecholates of most transition and main-group metals have long been known,³ and most of them have been described in detail.^{4,5} It is therefore surprising that there are only a few papers describing nickel catecholates, and most of these often partially contradictory reports date back over 50 years.^{6–11}

Due to their magnetic properties, complexes of Ni(II) and semiquinone¹² or quinone-type ligands have been better studied.^{5,10,13} The crystal structure of the square-planar Ni(II)

bis(3,5-*tert*-butylsemiquinone) is an example.¹⁴ A variety of ternary complexes containing Ni(II) catecholate moieties are known,¹⁵ but their properties are generally only remotely related to those of the binary compounds to be described here.

The first report of a Ni catecholate is a 1920 paper by Weinland and Döttinger,⁶ who described three complexes of interest. The first was a pale green compound defined as $\text{Na}_2[\text{Ni}(\text{cat})_2] \cdot \text{Na}_4[\text{Ni}(\text{cat})_3] \cdot 18\text{H}_2\text{O}$ (cat = catecholate dianion, $o\text{-C}_6\text{H}_4\text{O}_2^{2-}$) formed by reaction of Ni(II) acetate, catechol, and NaOH in an alcohol–water mixture. Characterization of this and the other compounds was by elemental analysis. The second was a dark green Ni bis(catecholate), $\text{Na}_2[\text{Ni}(\text{cat})_2] \cdot 12\text{H}_2\text{O}$, formed by the same ratio of reactants in water. The morphology of these crystals was described in detail (*vide infra*). No special attempts to exclude air during the syntheses were mentioned, although the performance of these reactions in a stoppered flask and the air sensitivity of the complexes were noted. The third Ni catecholate reported by these authors was a pale green amorphous “basic Ni catecholate” (basisches Ni-brenzcatechinat) of the empirical composition $\text{Ni}_3(\text{cat})_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, prepared by heating catechol with Ni(II) as its acetate in water. The formation

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of other (amorphous) Ni catecholates with complex compositions and the difficulties and frustrations associated with attempts to form well-defined (crystalline) Ni catecholates were described.^{8,9,16} In 1922, Reihlen essentially confirmed the synthesis of the disodium bis(catecholato)nickel(II) dodecahydrate, which he formulated as $\text{Na}_2[\text{Ni}(\text{cat})_2(\text{H}_2\text{O})_2] \cdot 10\text{H}_2\text{O}$.⁷ By means of conductivity measurements he also established the dianionic nature of the complex anion.

In what can be described as the first of the modern reports, a 1965 paper by Holm and co-workers included the preparation, polarographic data, and UV-vis spectrum of Ni(II) bis(catecholate) as its bis(tetra-*n*-propylammonium) salt, its corresponding perchlorinated catecholate analogue, and the bis(phenanthren-9,10-diolato)nickel(II) complex.¹⁰ None of these compounds were structurally characterized. Their colors were described as brown (catecholates) or dark red (phenanthrendiolates), and a tentative analysis of their electronic spectra was presented, with both types of complex found to be diamagnetic. This, in analogy with known Ni(II) β -diketonato complexes, led to the conclusion that these complexes are monomeric square-planar complexes. A procedure for the synthesis of Ni(II) bis(3,5-*tert*-butylsemiquinone), published in 1978 by Razuvaev, involves the oxidation of the corresponding bis(catecholate) complex, but this yellow and reportedly very air-sensitive intermediate was not characterized.¹² Most recently, Fish and co-workers prepared a Ni(II) complex of the bis-bidentate ligand 1,7-bis(2,3-dihydroxybenzoyl)-1,7-diazheptane (5-LICAM) as its cesium salt and reported its X-ray crystal structure.¹¹ This yellow diamagnetic complex contains a Ni bis(catecholate) moiety. However, there was little discussion with the previous unsubstituted catecholate chemistry. We had shown earlier that LICAM and the closely related 2,3-dihydroxyterephthalamide ligands are, due to the presence of electron-withdrawing functionalities on the catecholate ring, more acidic and have different complex binding constants.¹⁷ In addition, their metal complexes are much more resistant toward oxidation as compared to those of catechol.¹⁷ Lack of structural data for Ni(II) catecholates notwithstanding, their complex-forming constants have been determined in aqueous solution to be $K_1 = 8.6$ and $K_2 = 6.2$ (25 °C, 0.1 M ionic strength), and the formation of 1:2 metal to ligand complexes has been confirmed.^{18–20} Catecholates, as exemplified by the high-spin nature of the d^5 Fe(III) tris(catecholate) complex, are regarded as weak-field ligands.²¹ In this light it seems surprising that the catecholates reported by Holm and co-workers¹⁰ and the 2,3-dihydroxyben-

zoyl derivatives reported by Fish and co-workers¹¹ form diamagnetic square-planar complexes with Ni(II).

Because of the discrepancies in the literature and our long-standing interest in transition-metal complexes of catechol, we set out systematically to investigate the formation and properties of Ni(II) catecholates. We report here the synthesis, isolation, and X-ray structural determination of an octahedral paramagnetic Ni(II) *trans*-diaquo bis(catecholate), as well as the corresponding square-planar diamagnetic Ni(II) bis(catecholate). We also describe the physical and chemical properties of these Ni complexes. We can now account satisfactorily for the previous observations reported in the literature and can add some additional insight to the electronic properties of catecholate as a ligand, particularly its unusual behavior with Ni(II).

Experimental Section

Physical Measurements. UV-vis spectra were measured with an HP 8452A photodiode array or a Varian Cary 5G double-beam spectrophotometer in the solvents indicated. IR spectroscopy was performed on a Nicolet 550 spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-300 spectrometer; chemical shifts are reported on the δ scale in ppm relative to TMS and were calibrated against residual solvent peaks. Elemental analyses were performed at the facilities of the College of Chemistry, UC Berkeley. The SQUID measurements were taken on a Quantum Design MPMS system.

Synthesis of Compounds. All operations were carried out under an N₂ atmosphere by standard Schlenk or glovebox techniques. All chemicals were of reagent grade and were, after deoxygenation, used as received.

Na₂[*trans*-(H₂O)₂Ni^{II}(cat)₂]·12H₂O (1a). Under oxygen-free conditions, catechol (2.22 g, 20.2 mmol) and 2.48 g (10 mmol) of Ni^{II}(acetate)·4H₂O were each dissolved in separate containers in water (20 mL each). The solutions were combined, and 5 M aqueous NaOH (12 mL) was added slowly with stirring. The resulting yellow, clear solution was set aside. Crystallization set in generally within 1 h. After filtration, washing with small amounts of EtOH and Et₂O, and drying (without vacuum!), light green crystals (4.4 g, 77% yield) were obtained. Depending on the rate at which they precipitated, their habit ranged from thin plates to small clear blocks. Isolated yields were typically >80%: IR (KBr pellet) ν 3643 (s), 3512 (s), 3575 (s), 3027 (m), 3020 (br s), 1605 (s), 1486 (s), 1439 (m), 1310 (w), 1253 (m), 1031 (w), 870 (w), 808 (w), 751 (w), 655 (w) cm⁻¹. Anal. Calcd (found) for C₁₂H₃₆O₁₈Na₂Ni: C, 25.15 (25.13); H, 6.33 (6.29).

Na₂[(H₂O)₂Ni^{II}(cat)₂]·2EtOH·4.5H₂O (1b). This compound was prepared as described for 1a, with the exception that EtOH was added slowly to the clear aqueous solution of the complex until fine, light green mica-like crystals precipitated: yield 85%; ¹H NMR (300 MHz, DMSO-*d*₆, 100 °C) δ 5.7 (br m, 1H), 5.8 (br m, overlapping, 1H); IR (KBr pellet) ν 3544 (s), 3200 (s, broad), 3048 (s), 2970 (s), 2990 (s), 1656 (w), 1568 (m), 1496 (s), 1444 (m), 1328 (m), 1248 (s), 1206 (m), 1103 (m), 1041 (w), 871 (m), 793 (w), 741 (m) cm⁻¹. Anal. Calcd (found) for C₁₆H₃₃O_{12.5}Na₂Ni: C, 36.25 (36.24); H, 6.27 (6.27).

Na₂[Ni^{II}(cat)₂]·2DMF (2). Complex 1a or 1b was, under oxygen-free conditions, dissolved in warm DMF. Diethyl ether was allowed to diffuse into the slightly pink solution. Thin light pink rhombic crystals of 2 deposited over time: ¹H NMR (300 MHz, DMSO-*d*₆) δ 2.77 (s, 3H), 2.94 (s, 3H), 5.7 (br m, 4H), 5.75 (overlapping m, 4H), 7.98 (s, 2H); IR (KBr pellet) ν 1655 (s), 1563 (m), 1485 (s), 1442 (m), 1414 (m), 1383 (m), 1341 (w), 1322 (w), 1260 (s), 1141 (w), 1099 (m), 1063 (w), 1017 (m), 908 (m), 873 (m), 799 (m), 670 (s), 684 (w), 662 (m), 646 (m) cm⁻¹. Anal. Calcd (found) for C₁₈H₂₂N₂O₆Na₂Ni: C, 46.29 (45.88); H, 4.75 (4.77); N, 6.00 (5.81).

Na₂[Ni^{II}(cat)₂]·0.25H₂O (3). Either 1a or 1b was heated (50 °C) and vacuum was applied (10 mTorr) until no weight change corresponding to loss of the solvate molecules could be detected (after ~24 h). In either case, this treatment produced 3 in quantitative yield as a yellow powder: IR (KBr pellet) ν 3048 (w), 2996 (w), 1579 (w), 1488 (s), 1444 (w), 1318 (w), 1263 (s), 1108 (w), 1020 (w), 865 (w), 736

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Table 1. Summary of Crystallographic Data for $\text{Na}_2[\text{Ni}(\text{H}_2\text{O})_2(\text{cat})_2] \cdot 12\text{H}_2\text{O}$ (**1**) and $\text{Na}_2[\text{Ni}(\text{cat})_2] \cdot \text{DMF}$ (**2**)

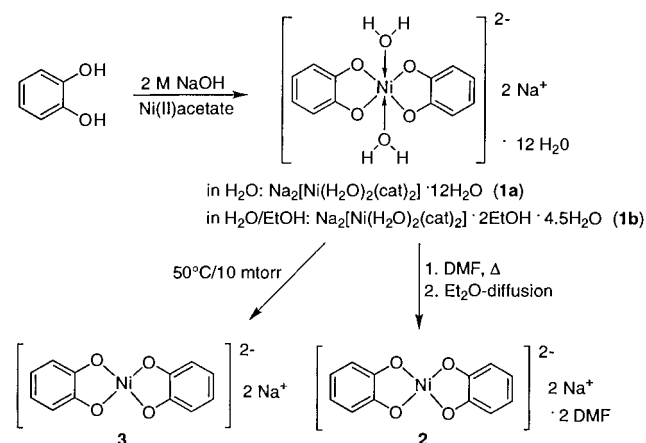
compd	$\text{Na}_2[\text{Ni}(\text{H}_2\text{O})_2(\text{cat})_2] \cdot 12\text{H}_2\text{O}$ (1)	$\text{Na}_2[\text{Ni}(\text{cat})_2] \cdot \text{DMF}$ (2)
formula	$\text{C}_{12}\text{H}_{36}\text{Na}_2\text{NiO}_{18}$	$\text{C}_{15}\text{H}_{15}\text{N}_2\text{Na}_2\text{NiO}_5$
mw	573.09	393.97
cryst size, mm	$0.30 \times 0.15 \times 0.07$	$0.40 \times 0.20 \times 0.05$
cryst syst;	monoclinic; <i>C</i> centered	monoclinic; primitive
lattice type		
space group	<i>C2/c</i> (No. 15)	<i>P2₁/m</i> (No. 11)
<i>a</i> , Å	26.0287(8)	6.0906(5)
<i>b</i> , Å	9.0016(3)	13.208(1)
<i>c</i> , Å	10.6992(3)	12.826(1)
β , °	101.809(1)	95.711(1)
<i>Z</i> ; <i>V</i> , Å ³	4; 2453.8(1)	2; 1026.7(1)
<i>D</i> _{calcd} , g/cm ³	1.551	1.274
$\mu(\text{Mo K}\alpha)$, cm ⁻¹ ;	9.04; -149	10.06; -103
temp, °C		
total (unique) no. of rflns; <i>R</i> _{int}	5125 (1869); 0.069	5170 (1905); 0.034
no. of rflns with <i>I</i> ≥ 3σ(<i>F</i> ²)	1358	1341
no. of variables	147	184
final <i>R</i> ; <i>R</i> _w ; <i>R</i> _{all} ^a	0.046; 0.063; 0.059	0.033; 0.039; 0.055
GOF	1.86	1.30
min/max res e densities, e Å ⁻³	-0.51; 0.83	-0.40; 0.26

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}.$$

(m), 741 (m) cm⁻¹. Anal. Calcd (found) for $\text{C}_{12}\text{H}_{36}\text{O}_{18}\text{Na}_2\text{Ni}$: C, 44.30 (44.36); H, 2.63 (2.85).

X-ray Crystallographic Studies. Suitable crystals of **1** and **2** were mounted on a quartz fiber using Paratone N hydrocarbon oil. The crystallographic data sets were collected on a Siemens SMART diffractometer equipped with a CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å).²² Area detector frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° per frame and a total measuring time of 20 s each. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the measured positions of 3479 (**1**) and 3093 (**2**) reflections, respectively. Data were integrated using SAINT²³ to a maximum 2θ value of 46.5° (**1**) and 52.1° (**2**). The data were corrected for Lorentz and polarization effects. No decay corrections were applied. An empirical absorption correction for **1** was based on the measurement of redundant and equivalent reflections using an ellipsoidal model for the absorption surface and was applied using XPREP.²⁴ Such an absorption correction for **2** was applied using SADABS.²⁵ Equivalent reflections were merged. The space groups were determined on the basis of systematic absences, packing considerations, statistical analyses of intensity distributions, and the successful solution and refinement of the structures. The structures were solved by direct methods.²⁶

The non-hydrogen atoms for both **1** and **2** were refined anisotropically. For **1** the hydrogen atoms were included in calculated, idealized positions, while for **2** the positions of the hydrogen atoms were refined and the isotropic thermal parameters held fixed. All calculations were performed using the teXsan crystallographic software package.²⁷ Further experimental details and the crystal data are listed in Table 1. A detailed report of the X-ray crystal structure determination, including final

Scheme 1

coordinates, temperature factors (U_{eq}), bond lengths and angles, and non-bonded contact distances have been deposited with the Cambridge Crystallographic Database (reference number 970925B).

Results and Discussion

Synthesis of the Nickel(II) Catecholates. The addition of up to 2 equiv (based on catechol) of 5 M aqueous NaOH to a concentrated aqueous solution of catechol and Ni(II) as its acetate in a 2:1 ratio under an oxygen-free atmosphere resulted instantly in the formation of a thick, off-white creamy precipitate. Slow addition of at least 2 equiv more of base resulted in the dissolution of this precipitate to produce a clear yellow-green solution. Upon standing, crystals deposited within 48 h at ambient temperature. Depending on the rate of crystallization, thin plates or more coarse light green crystals, which analyzed as $\text{C}_{12}\text{H}_{36}\text{O}_{18}\text{Na}_2\text{Ni}$ (the expected (hydrated) Ni(II) bis(catecholate) disodium salt), formed (Scheme 1). The UV-vis spectrum (vide infra) indicated catecholate coordination of the Ni(II) center. The IR spectrum (KBr pellet) showed strong signals at 1605, 1486 (aromatic ring stretch), 1439, and 1253 cm⁻¹ (C—O stretch), typically attributed to the coordinated catecholate moiety.²⁸ Next to these were bands assigned to ordered hydrogen-bonded H₂O (signals at 3643, 3612, and 3575 cm⁻¹) and interstitial water (broad signal centered at 3020 cm⁻¹) overlaid with signals for the aromatic C—H stretch (3027, 3002 cm⁻¹).

Fast crystallization could be induced by the addition of EtOH, and the silver-green mica-like crystals of **1b** generated by this procedure analyzed for the Ni bis(catecholate) solvated by H₂O and EtOH. Solutions of **1** in D₂O were paramagnetic, based on their broadened and extremely shifted ¹H NMR signals (~25 ppm). (For a detailed investigation of the magnetic moment of **1** see below.) The analytical and spectral data corroborated the assignment of the coordination sphere of the Ni(II) center as being octahedral. This assignment was ultimately proven by the X-ray structure of this compound (*vide infra*).

Dissolution of **1** in hot (>100 °C) DMSO-*d*₆ generated a slightly pink solution that was diamagnetic, as demonstrated by its ¹H NMR spectrum (300 MHz): δ 5.7 (br m, 1H); 5.8 (br m, overlapping, 1H). Slow vapor diffusion of Et₂O into a DMF solution of **1** deposited pink crystals suitable for analysis by X-ray crystallography (*vide infra*). Elemental analysis corresponded to $\text{Na}_2[\text{Ni}^{\text{II}}(\text{cat})_2] \cdot 2\text{DMF}$ (**2**). The IR, again, indicated the presence of coordinated catecholate moieties (among others,

(22) SMART: Area-Detector Software Package; Siemens Industrial Automation, Inc., Madison, WI, 1995.

(23) SAINT: SAX Area-Detector Integration Program; Siemens Industrial Automation, Inc., Madison, WI, 1995.

(24) XPREP: Part of the SHELXTL Crystal Structure Determination Package; Siemens Industrial Automation, Inc., Madison, WI, 1995.

(25) SADABS: Siemens Area Detector Absorption Correction Program; G. Sheldrick, advance copy, 1996.

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(27) teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985, 1992.

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bands at 1442 and 1260 cm^{-1}) and proved the presence of DMF (1655 cm^{-1} , s, $\nu(\text{C}=\text{O})$). These data characterized the complex as square-planar Ni(II) bis(catecholate). As shown below, this is also confirmed by the X-ray crystal structure analysis of **2**.

Application of high vacuum and gentle heating (10 mTorr, 50 °C) of a measured quantity of **1a** or **1b** resulted in the formation of a yellow powder (**3**) with a weight corresponding to that of the starting material without the molecules of solvation. However, elemental analyses showed the presence of up to 0.25 mol of residual H_2O . Application of higher temperatures led to visible darkening of the material, indicating the onset of decomposition. The IR of this compound was correspondingly simplified as compared to that of **1**. The observed color change upon dehydration is one indication for the involvement of H_2O in the coordination sphere of Ni, with the change in the magnetic moment of the compound upon dehydration being another (*vide infra*).

The formation of Ni(II) catecholates as their bis(pyridinium)¹⁶ or ethylenediammonium salts²⁹ (by the addition of the bases to aqueous solutions containing Ni(II) salts) has been published. In both cases, the compounds were described as blue-green, air-stable powders. Both are also characterized by their near-insolubility in H_2O . We were able to reproduce the reported results, including the elemental analyses indicating roughly the proper composition. However, in comparison with the characteristics of the Ni(II) catecholates **1** and **2**, the color and air stability of these complexes indicated that they were not pure Ni(II) catecholates but rather (probably polymeric) mixed-ligand species.

Magnetic Measurements. In the solid state the Ni bis(catecholate) **1a** exhibits a field-independent (SQUID at 5000 and 40000 G) regular paramagnetism ($\mu_{\text{eff}} = 2.93 \mu_{\text{B}}$ at 300 K; linear dependence of $1/\chi_{\text{m}}$ vs T between 5 and 300 K, $r^2 = 0.978$). This value is close to the expected spin-only value for a system with $S = 1$ ($2.83 \mu_{\text{B}}$), consistent with a d^8 complex in an octahedral environment.

The compounds **2** and **3** are diamagnetic.³⁰ The diamagnetism indicates the loss of the axial ligands (water) of the octahedral species and the formation of a square-planar Ni(II) low-spin complex. Such solvent-dependent interchange of the coordination sphere, and change in magnetic moment, has precedent in the properties of the so-called anomalous Ni(II) complexes,³¹ in particular the N,N'-disubstituted stilbene salts of Ni(II), also known as the Lifschitz salts.³² Addition of pyridine- d_5 to the warm solution does not result in a severe shift and broadening of the catecholate proton signals, indicating that no paramagnetic species form upon addition of this potential ligand.

UV-Vis Spectra. The tentatively assigned UV-vis spectra of a square-planar as well as a (on the basis of the interpretation of the UV-vis spectrum) distorted-octahedral Ni(II) bis(catecholate) have been reported in the literature in two independent investigations.^{10,29} While confirming the results obtained for the square-planar complex, we measured a significantly different spectrum for the octahedral species **1**.

Next to the strong band assigned to a $\pi-\pi^*$ transition of the ligand at 212 and 256 nm ($\epsilon = 9400$ and 9600) nm, three low-intensity bands attributable to d-d transitions at 402, 740 (sh), 766, 853, and 974 nm ($\epsilon = 200, 20, 25,$ and 275) are observed for an aqueous solution of **1** (in the range 200–1000 nm). This is consistent with an octahedral coordination of the d^8 central metal.³³ This, in turn, shows that the structure of **1** observed in the solid state is preserved in solution. Sandhu *et al.* analyzed the UV-vis spectrum of a Ni(II)-catechol solution to ascertain the stereochemistry around the metal and reported bands at 465, 662, 740, and 1140 nm.²⁰ In comparison, to our data, the authors appear to have had a different species in hand. Due to the absence of experimental data (e.g. metal to ligand ratio, cation, pH of the solution), no further conclusions can be drawn. However, their inference of the stereochemistry of Ni(II) catecholate in aqueous solution is, perhaps coincidentally, analogous to our finding. Sandhu *et al.* also report that no significant shifts of the absorption bands of the complex are observed upon heating to 50 °C.²⁰ Consistent with this observation, we have found that, on the basis of VT NMR studies in D_2O , no diamagnetic species can be observed upon heating the sample up to 90 °C. This shows that the stereochemistry around the metal essentially remains unchanged in the temperature range investigated.

The UV-vis spectrum of a DMF solution of the square-planar species **2** (in the window between 400 and 1100 nm) exhibits two pairs of low-intensity bands at 530 and 686 ($\epsilon = 100$ and 60), attributed to the first lowest energy spin-allowed ligand field absorptions of Ni(II) in a square-planar coordination environment, and an additional pair of low-intensity absorption bands at 915 and 1020 nm ($\epsilon = 30$ and 25). Therefore, the solid-state structure of **2** is also maintained in solution. Holm and co-workers pointed out that, for the square-planar Ni(II) case, the catecholate ligand lies more to the weak field end of the spectrochemical series than do, for instance, the β -diketonates.¹⁰ This observation now finds its structural confirmation in the existence of the octahedral high-spin complex **1**.

In the spectra of neither **1** nor **2** are bands observed that could be due to ligand-to-metal charge transfer. Although the spectra of the catecholates of, for instance, Ti(IV) or Fe(III) are dominated by such bands, their absence in the Ni(II) catecholates is, due to the low charge of the central metal and the instability of the Ni(I) oxidation state, expected.

Crystal Morphology and X-ray Crystal Structures. As indicated above, Weinland and Döttinger described in their 1920 report the morphology of dark green blocks with the empirical formula $\text{Na}_2[\text{Ni}(\text{cat})_2] \cdot 12\text{H}_2\text{O}$. They were found to be monoclinic prismatic, with $a:b = 1.19$ (c could not be determined) and $\beta = 112.5^\circ$ with profound mica-like splitting behavior along the [001] plane, also parallel to the [100] and [010] planes.⁶ This proclivity was reported to increase with progressing deterioration of the crystals. We can confirm all these observations with the exception that the crystals are, when prepared under an inert-gas atmosphere, very light green (and that we determined the total number of coordinated waters and waters of crystallization to be 14; *vide supra*). Upon exposure to air, the light green crystals decay within hours, turning dark green to black, initially without losing their structural integrity or shine.

Complex **1** crystallizes in the monoclinic space group $C2/c$ (No. 5). Table 1 lists further experimental details of the X-ray structure determinations of **1** and **2**. Table 2 lists the atomic coordinates and B_{eq} values for selected atoms. The nickel ion is located on a crystallographic inversion center in a slightly

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(30) The dehydrated compound **3** continues to show a small magnetic moment, which varies with the mode of preparation of the sample. Hence, we conclude that this paramagnetism is due to residual amounts of **1** (or other paramagnetic impurities).

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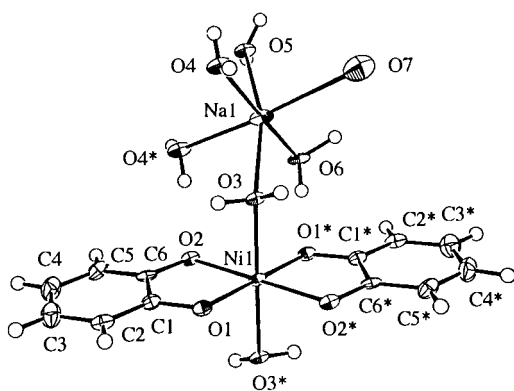
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Table 2. Final Values of Refined Atomic Coordinates and B_{eq} Values (\AA^2) for the Non-Hydrogen Atoms in $\text{Na}_2[\text{Ni}(\text{H}_2\text{O})_2(\text{cat})_2] \cdot 12\text{H}_2\text{O}$ (**1**)

atom	x	y	z	B_{eq}^a
Ni(1)	0.2500	0.2500	0.5000	1.06(2)
Na(1)	0.30737(7)	0.6750(2)	0.4854(2)	1.98(4)
O(1)	0.1937(1)	0.2336(3)	0.6074(3)	1.32(6)
O(2)	0.1919(1)	0.3613(4)	0.3785(3)	1.30(6)
O(3)	0.2740(1)	0.4620(3)	0.5878(3)	1.51(7)
O(4)	0.2831(1)	0.8311(4)	0.6390(3)	1.78(7)
O(5)	0.3156(1)	0.8907(4)	0.3708(3)	1.67(7)
O(6)	0.3328(1)	0.5348(4)	0.3281(3)	1.83(7)
O(7)	0.4148(2)	0.7154(5)	0.5699(4)	4.4(1)
O(8)	0.4357(2)	0.6292(6)	0.3310(4)	4.1(1)
O(9)	0.5000	0.4223(9)	0.2500	4.7(2)
C(1)	0.1477(2)	0.2896(6)	0.5426(4)	1.17(9)
C(2)	0.1020(2)	0.2839(6)	0.5905(4)	1.8(1)
C(3)	0.0547(2)	0.3434(7)	0.5198(5)	2.3(1)
C(4)	0.0541(2)	0.4085(7)	0.4027(5)	2.3(1)
C(5)	0.0993(2)	0.4144(6)	0.3542(4)	2.05(10)
C(6)	0.1469(2)	0.3564(5)	0.4214(4)	1.24(9)

$$^a B_{\text{eq}} = \frac{8}{3}\pi^2[U_{11}(a^*)^2 + U_{22}(b^*)^2 + U_{33}(c^*)^2 + 2U_{12}a^*b^* \cos \gamma^* + 2U_{13}a^*c^* \cos \beta^* + 2U_{23}b^*c^* \cos \alpha^*].$$

**Figure 1.** ORTEP plot of the molecular structure of $\text{Na}_2[\text{Ni}(\text{H}_2\text{O})_2(\text{cat})_2] \cdot 12\text{H}_2\text{O}$ (**1**) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

distorted octahedral environment composed of two symmetry-equivalent catechol ligands in the equatorial plane and two axial water molecules (Figure 1). The bond lengths of the two catechol oxygens are identical ($\text{Ni}(1)\text{—O}(1) = 2.045(3)$ and $\text{Ni}(1)\text{—O}(2) = 2.043(3)$ \AA). The $\text{Ni}(1)\text{—O}(3)$ distance to the axial water oxygen is slightly longer, at 2.162(3) \AA . Selected bond distances and angles are listed in Table 4. These observed bond lengths compare well with those observed in other octahedral high-spin Ni(II) complexes.³⁴

Infinite chains, formed by the axial ligands, which are linked to hexacoordinate Na ions through bridging water molecules, run along the *b* axis of the unit cell (Figure 2). The Na ion is effectively octahedrally coordinated by water molecules, three of which are bridging: one water molecule bridges to Ni(1), and two of the waters are symmetry-equivalent and bridge to a symmetry-equivalent Na ion. The remaining three water molecules are terminal. One of these Na—O bonds is quite long ($\text{Na}(1)\text{—O}(7) = 2.780(5)$ \AA), while the other two are shorter ($\text{Na}(1)\text{—O}(5) = 2.330(4)$ \AA and $\text{Na}(1)\text{—O}(6) = 2.306(4)$ \AA). Additional non-coordinated water molecules are present and occupy channels that run along the *c* direction. The hydrogen atoms of the interstitial water molecules were not found.

Complex **2** crystallizes in the monoclinic space group $P2_1/m$ (No. 11). Table 2 lists the atomic coordinates and B_{eq} values

Table 3. Final Values of Refined Atomic Coordinates and B_{eq} Values (\AA^2) for the Non-Hydrogen Atoms in $\text{Na}_2[\text{Ni}(\text{cat})_2] \cdot 2\text{DMF}$ (**2**)

atom	x	y	z	B_{eq}^a
Ni(1)	0.0000	0.0000	0.0000	1.51(1)
Na(1)	0.4349(2)	-0.11301(9)	-0.05328(9)	1.69(3)
O(1)	-0.1125(3)	0.0293(2)	0.1260(2)	1.85(5)
O(2)	0.2804(3)	-0.0114(2)	0.0727(1)	1.67(4)
O(3)	0.3805(6)	-0.2500	-0.1669(3)	3.17(9)
O(4)	0.5459(6)	-0.2500	0.0591(3)	2.98(9)
N(1)	0.3483(7)	-0.2500	-0.3443(3)	2.60(9)
N(2)	0.8258(8)	-0.2500	0.1893(4)	3.4(1)
C(1)	0.0467(5)	0.0160(2)	0.2056(2)	1.57(6)
C(2)	0.0147(5)	0.0231(2)	0.3112(2)	1.67(7)
C(3)	0.1895(5)	0.0018(3)	0.3876(2)	2.02(7)
C(4)	0.3953(5)	-0.0241(2)	0.3587(2)	2.05(7)
C(5)	0.4299(5)	-0.0288(3)	0.2527(3)	1.71(7)
C(6)	0.2587(5)	-0.0079(2)	0.1769(2)	1.66(6)
C(7)	0.2679(9)	-0.2500	-0.2526(4)	2.6(1)
C(8)	0.582(1)	-0.2500	-0.3482(6)	4.1(2)
C(9)	0.207(1)	-0.2500	-0.4420(5)	3.4(2)
C(10)	0.6146(10)	-0.2500	0.1524(4)	2.7(1)
C(11)	0.896(2)	-0.2500	0.3005(7)	5.4(2)
C(12)	0.994(1)	-0.2500	0.1179(8)	5.2(2)

$$^a B_{\text{eq}} = \frac{8}{3}\pi^2[U_{11}(a^*)^2 + U_{22}(b^*)^2 + U_{33}(c^*)^2 + 2U_{12}a^*b^* \cos \gamma^* + 2U_{13}a^*c^* \cos \beta^* + 2U_{23}b^*c^* \cos \alpha^*].$$

Table 4. Selected Bond Distances (\AA) and Bond Angles (deg) for $\text{Na}_2[\text{Ni}(\text{H}_2\text{O})_2(\text{cat})_2] \cdot 12\text{H}_2\text{O}$ (**1**) and $\text{Na}_2[\text{Ni}(\text{cat})_2] \cdot 2\text{DMF}$ (**2**)

	1	2
Ni(1)—O(1)	2.045(3)	1.858(2)
Ni(1)—O(2)	2.042(3)	1.868(2)
Ni(1)—O(3)	2.162(3)	
Na(1)—O(1)*		2.365(2)
Na(1)—O(2)		2.363(2)
Na(1)—O(2)*		2.419(2)
Na(1)—O(3)	2.453(4)	2.326(2)
Na(1)—O(4)	2.345(4)	2.369(2)
Na(1)—O(4)*	2.457(4)	
Na(1)—O(5)	2.330(4)	
Na(1)—O(6)	2.305(4)	
O(1)—C(1)	1.352(6)	1.347(4)
O(2)—C(6)	1.345(5)	1.357(3)
C(1)—C(2)	1.389(7)	1.390(4)
C(2)—C(3)	1.410(7)	1.402(4)
C(3)—C(4)	1.380(8)	1.385(4)
C(4)—C(5)	1.380(7)	1.397(4)
C(5)—C(6)	1.399(7)	1.380(4)
C(6)—C(1)	1.425(6)	1.412(4)
O(1)—Ni(1)—O(2)	82.561	88.894
O(1)—Ni(1)—O(2)*	79.438	91.105
O(1)—Ni(1)—O(3)	89.807	
O(1)—Ni(1)—O(3)*	90.192	
O(2)—Ni(1)—O(3)	87.342	
O(2)—Ni(1)—O(3)*	92.627	
Ni(1)—O(1)—C(1)	110.255	109.381
Ni(1)—O(2)—C(6)	110.525	108.347
O(1)—C(1)—C(6)	118.072	116.083
O(2)—C(6)—C(1)	118.186	116.417
Ni(1)—O(2)—Na(1)		96.386
C(6)—O(2)—Na(1)		140.949

for selected atoms. The metal center is coordinated in a slightly distorted square planar fashion by two catecholate units and lies on a crystallographic inversion center (Figure 3). The Ni—O distances ($\text{Ni}(1)\text{—O}(1) = 1.858(2)$ \AA and $\text{Ni}(1)\text{—O}(2) = 1.868(2)$ \AA) are much shorter than the Ni—O bond distances observed in the high-spin complex **1**, consistent with the low-spin state of complex **2**. The measured values compare well with those for known square-planar Ni complexes with O donors.³⁴ The longer of the two Ni—O bond lengths corresponds to the oxygen atom which bridges between the Ni center and a Na atom (Na—

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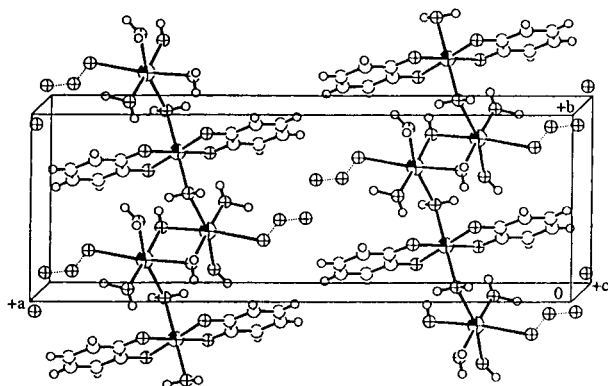


Figure 2. Oblique view of the unit cell for **1**, illustrating the infinite chain structure of the Na-bridged Ni(II) catecholate units and the intrachain solvate-filled channels.

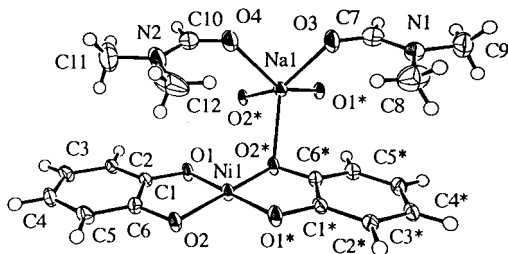


Figure 3. ORTEP plot of the molecular structure of $\text{Na}_2[\text{Ni}(\text{cat})_2] \cdot 2\text{DMF}$ (**2**) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

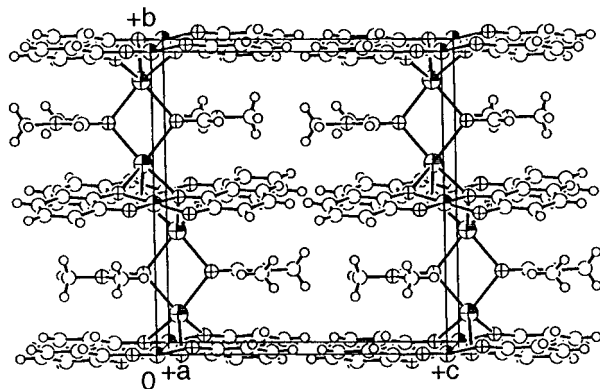


Figure 4. Oblique view of the unit cell for **2**, illustrating the infinite chain structure of the Na-bridged Ni(II) catecholate units, forming layers sandwiching the solvated Na atoms.

(1)). The coordination sphere of the pentacoordinated Na atom is further composed of one O atom of an adjacent Ni(II) bis(catecholate) unit and two DMF molecules. The latter bridge between another set of equivalently coordinated Na atoms. Thus, the structure forms infinite chains in the *b* direction, with layers of square-planar Ni(II) bis(catecholate) bridged through sodium ions to layers of DMF molecules (Figure 4).

The statistically significant deviations of the C–C bond lengths in the catecholate rings of both Ni catecholates from those found in catechol³⁵ are comparable to those observed in, for instance, the tris(catecholates) of V(III),³⁶ Cr(III) and Fe(III).³⁷ As in these examples, the deviations can be interpreted as a small contribution of a quinoid resonance form to the catecholate binding motif.

Chemical Reactivity. The Ni(II) catecholates **1** and **2** are very sensitive toward oxidation. Crystals of **1** darken quickly upon exposure to air and are entirely decomposed within 1 day. We found that their light green aqueous solutions are far more sensitive, turning dark brown-green within seconds of contact with air. This is similar to the catecholates of, for example, Cu(II). This reactivity reflects the diminished electronic stabilization the dicationic central metal can exercise on the electron-rich dianionic ligand as compared with the catecholates of Fe(III) and Ga(III) (moderately air-stable) and those of Ti(IV) (entirely air stable).³⁸

An aqueous solution of **1**, when mixed with morpholine and then exposed to air, forms in low yields (<20%) 4,5-dimorpholino-2,3-quinone, most likely *via* a stepwise oxidation–conjugate addition pathway typical for catechols. This potentially metal bridging ligand has been prepared before by a similar but more effective procedure (up to 64% yield; catechol, basic conditions, air oxidation and Cu(II) catalysis).³⁹

Conclusions

Our findings essentially confirm the reports by Weinland and Döttinger and Reihlen, although we cannot reproduce the formation of the alleged mixed $\text{Ni}(\text{cat})_2/\text{Ni}(\text{cat})_3$ species.^{6,7} Catecholate forms well-defined crystalline bis complexes with Ni(II) which, depending on their condition of formation, are diamagnetic (low spin) square-planar complexes (**2**, **3**) or paramagnetic (high spin) octahedral complexes (**1**) in which the axial positions are occupied by water molecules. This explains why contradicting accounts of high- and low-spin Ni(II) catecholates were described in the literature. We conclude that the authors of reports describing the alleged formation of air-stable Ni(II) bis(catecholates) as their bipyridinium¹⁶ or ethylenediammonium salts²⁹ were in error.

Catechol can be classified as a weak-field ligand.^{20,21} In fact, it has been compared in its coordination properties to the oxo dianion.⁴ In analogy to the octahedral coordination environment formed by six oxygens around the Ni(II) centers in the structures of NiO (NaCl structure)⁴⁰ and Ni(OH)₂ (Brucit structure),⁴⁰ the formation of the octahedral species **1** is not surprising. The formation of the Ni(II) catechol complex in aqueous solution has been determined to be endothermic.²⁰ This is typically the case for “entropy-stabilized” high-spin complex formations of a weak field ligand with a given metal. On the other hand, our study has unequivocally shown that the corresponding low-spin square-planar complex is also stable. Thus for Ni(II), catecholate is a borderline strong-/weak-field ligand and parallels in its coordination properties the ligands that form the so-called anomalous Ni(II) complexes, especially those stilbenediamines which are present in the Lifschitz salts.³²

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