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Synthesis, Structure, and Spectral Characterization of Nickel(II) (*R*,*R*)-Tartrate. Crystal and Molecular Structure of Polymeric Diaquabis((*R*,*R*)-tartrato-$O^1,O^2:O^3,O^4$)dinickel(II) Trihydrate at -162 °C

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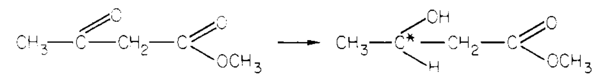
Hydrated nickel(II) (*R*,*R*)-tartrate has been synthesized and characterized with the use of ligand field and IR spectra. The crystal structure has been determined by single-crystal X-ray diffraction at -162 °C. The title compound crystallizes in the orthorhombic space group $P2_12_12$ with (at -162 °C) $a = 7.805$ (3), $b = 11.068$ (4), and $c = 8.974$ (8) Å. The unit cell contains two nuclear formula units of $Ni_2(C_4H_4O_6)_2(H_2O)_5$. The structure determination was performed by using diffractometer data (Mo Kα radiation) and standard heavy-atom techniques, followed by least-squares refinement. Each dimeric unit contains one (*R*,*R*)-tartrato dianion chelated to two nickel ions (Ni-Ni = 5.202 (1) Å), with the use of two hydroxy oxygen and two carboxyl oxygen atoms as donor atoms. A second tartrato dianion chelates in the same way to the same pair of nickel(II) cations. This tartrato dianion, however, also binds to two nickel ions of neighboring dimeric units through the other carboxyl oxygen atoms. The octahedral coordination geometry for each nickel ion is completed by such a carboxyl oxygen of a neighboring dimer and a water molecule. Ni-O distances vary from 1.979 (5) to 2.133 (6) Å, whereas the octahedral O-Ni-O angles are 78-104 and 160-172°. Additional water molecules are held in the crystal lattice, forming a hydrogen-bonding network of O-H-O-H linkages keeping the dimers together in nonplanar sheets. The octahedral Ni-O geometry agrees with the ligand field spectrum in the solid state, whereas infrared spectra confirm the presence of coordinated tartrate ligands and the extensive hydrogen bonding. The dimeric units are packed in the crystal lattice in a manner somewhat related to that of the corresponding Cu(II) compound. The structure is discussed in view of the use of the title compound in asymmetric catalytic reactions, such as the hydrogenation of methyl 3-oxobutanoate.

Introduction

For more than a century nickel metal has been known to be a very active hydrogenation catalyst.[1] As Raney nickel, or supported on pumice, silica, or alumina, nickel has been used extensively to catalyze the hydrogenation of C=C, C=O, and similar bonds in unsaturated organic molecules.[1] It has been found that such nickel catalysts can be modified by immersion in an aqueous solution of an asymmetric amino or hydroxy acid. By this treatment the catalyst acquires the property known as enantioselectivity;[2] i.e., in the hydrogenation of molecules with a prochiral carbon atom the two possible stereoisomers are formed in significantly different quantities. Catalysts with high enantioselectivity, for instance in the hydrogenation reaction of methyl 3-oxobutanoate



have been prepared by "modifying" nickel catalysts with optically active tartaric acid.[3] Previously, Hoek and Sachtler[4] published evidence suggesting that the modification process is a corrosive chemisorption, resulting in the formation of nickel tartrate complexes adhering to the catalyst surface. Such complexes are supposed to serve as enantioselective sites, e.g. molds on the catalyst surface where the stereospecific adsorption and/or the stereoselective reaction of the substrate molecules can take place.[5] Since pure nickel tartrate (or sodium nickel tartrate) is unable to catalyze hydrogenation in the absence of metallic nickel, a dual-site mechanism is proposed. Hydrogen is dissociated on the surface of nickel metal particles, followed by migration of H atoms to the tartrate complex, where they become attached to the adsorbed substrate molecule in two separate steps. This model suggests that the Ni atoms in the nickel tartrate complexes serving as catalytic sites have two vacant ligand positions available for adsorbed hydrogen and substrate, respectively. A more precise knowledge of the structure of these complexes might be useful in understanding the high enantiomeric excess obtained with these catalysts. Such information will also be of help in understanding the action of certain comodifiers, found to improve the selectivity further, without impairing activity.[6] In the absence of structure data for these surface complexes, assumptions had to be made. Generally, surface complexes resemble those in three-dimensional crystals; therefore, the structure of the surface tartrate had been assumed to be similar to that of dinuclear antimony, vanadium, and copper tartrate complexes.[7] Evidence of the existence of dimeric nickel tartrate complexes in aqueous solutions has been put forward.[8] Hoek suggested that the formation of both the two-dimensional surface layers and the three-dimensional crystals out of the dimers (consisting of two nickel atoms with two tartrate ions) as building blocks should be possible. The coordinatively unsaturated nickel ions required in the dual-site model for the hydrogenation are assumed to result from imperfections in the two-dimensional array of the dimeric building blocks. The comparison of nickel tartrate with copper tartrate, for which a crystal structure determination has been reported,[7] may be useful; however, X-ray powder diffraction data[9] and infrared spectra[10] have shown that the two compounds are not iso-

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(1) Berkman, S.; Morrell, J. C.; Egloff, G. In "Catalysis"; Reinhold: New York, 1946; and references therein.

(2) Izumi, Y.; Tai, A. "Stereo-differentiating Reactions"; Academic Press: New York, 1971.

(3) (a) Izumi, Y.; Imaida, M.; Fukawa, H.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 155. (b) Harada, T.; Yamamoto, M.; Onaka, S.; Imaida, M.; Ozaki, H.; Tai, A.; Izumi, Y. *Ibid.* **1981**, *54*, 2323.

(4) (a) Hoek, A.; Sachtler, W. M. H. *J. Catal.* **1979**, *58*, 276. (b) Hoek, A.; Woerde, H. M.; Sachtler, W. M. H. *Stud. Surf. Sci. Catal.* **1981**, *7*, 376.

(5) Hoek, A. Ph.D. Thesis, Leiden State University, 1982.

(6) Sachtler, W. M. H. *Faraday Discuss. Chem. Soc.* **1981**, *72*, 28.

(7) (a) Kiosse, G. A.; Golovastinov, N. I.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1964**, *155*, 545. (b) Forrest, J. G.; Prout, C. K. *J. Chem. Soc. A* **1967**, 1312. (c) Prout, C. K.; Carruthers, J. R.; Rossoti, F. J. C. *Ibid.* **1971**, 3336.

(8) (a) Hoffman, H.; Nickel, U. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 1096. (b) Hoffman, H.; Ulbricht, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1970**, *25B*, 1327.

(9) (a) Hanawalt, J. D.: Rinn, H. W.; Frevel, L. K. *Ind. Eng. Chem., Anal. Ed.* **1938**, *10*, 487. (b) Kubecova, K.; Frei, V. *Collect. Czech. Chem. Commun.* **1969**, *34*, 1141.

(10) (a) Bolard, J., *J. Chim. Phys. Phys.-Chim. Biol.* **1965**, *62*, 900. (b) Carillo, A.; Vieles, P.; Bonniol, A. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1972**, 912.

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Table I. Summary of Crystal and Experimental Data for $Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_5$

formula	$C_8H_{18}Ni_2O_{17}$
fw	503.6
cryst dimens, mm^3	0.22 × 0.12 × 0.05
space group	orthorhombic, $P2_12_12$
a, Å	7.805 (3) (7.852 (2)^a)
b, Å	11.068 (4) (11.102 (3)^a)
c, Å	8.974 (8) (9.030 (2)^a)
V, Å^3	775.3 (787.2^a)
Z	2
density (calcd), g cm^{-3}	2.04
density (obsd), g cm^{-3}	2.09
temp, °C	−162
λ(Mo Kα), Å	0.71073
monochromator	graphite
μ(Mo Kα), cm^{-1}	25.34
θ range, deg	2–25 ($+h, \pm k, \pm l$)
max scan time/reflecn, s	90
scan mode	ω–θ
no. of indep reflecns	2639
no. of reflecns used ($I > 2\sigma(I)$)	2083
no. of param refined	156
final *R*	0.026^b
final R_w	0.033^b
weighting	$1/w = (\sigma(F_o))^2 + (0.023\|F_o\|)^2$

^{a} 20 °C. ^{b} $R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma F_o$ and $R_w = (\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w F_o{}^2)^{1/2}$.

morphous. Therefore, we decided to determine the crystal structure of nickel tartrate to assist us in our studies of enantioselective hydrogenation. A suitable single crystal could only be grown from warm aqueous solutions. Because of the small dimensions of the crystals and the need to obtain detailed structural information (including hydrogen bond interactions, which Yasumori proved to play an important role in these asymmetric reactions[11]), the X-ray analysis was performed at low temperature.

Experimental Section

Materials. (*R*,*R*)-(+)-Tartaric acid (*d*-tartaric acid (Aldrich)), $Na_2(d\text{-}C_4H_4O_6)(H_2O)_2$ (Merck), $Cu(NO_3)_2(H_2O)_3$ (Merck), $NiSO_4(H_2O)_6$ (Merck), and water glass (Merck) were commercially available.

Preparation. $Ni_2((R,R)\text{-}(+)\text{-}C_4H_4O_6)_2(H_2O)_5$. An aqueous solution of sodium *d*-tartrate ($Na_2((R,R)\text{-}(+)\text{-}C_4H_4O_6)$) and nickel(II) sulfate was slowly heated to 70 °C, and kept at this temperature for 16 h. A greenish microcrystalline precipitate formed, which was washed with ethanol and diethyl ether and dried. In the precipitate small nickel(II) (*R*,*R*)-(+)-tartrate crystals were present. Anal. Calcd for $C_8H_{18}Ni_2O_{17}$: C, 19.08; H, 3.60; Ni, 23.3; O, 54.0. Found: C, 19.17; H, 3.62; Ni, 24.3; O, 52.7.

$Cu((R,R)\text{-}(+)\text{-}C_4H_4O_6)(H_2O)_3$. Crystalline copper(II) (*R*,*R*)-(+)-tartrate was prepared in silica gel.[12] The gels were prepared by adding an aqueous solution of (*R*,*R*)-(+)-tartaric acid to a solution of water glass (density 1.05 g cm^{-3}). After the gels were formed, a copper(II) nitrate solution was placed on top to allow slow diffusion of copper ions into the gel. A crystalline product was formed. The crystals were taken from the gel, washed with ethanol and diethyl ether, and dried in air.

Measurements. Diffuse-reflectance spectra were recorded on a Beckman DK-2A spectrophotometer with MgO as reference. Infrared spectra were recorded on a Perkin-Elmer Model 580 spectrophotometer using KBr disks and Kel-F mulls. X-ray powder diffraction patterns were registered with a Nonius Guinier-de Wolff camera, using Cu Kα radiation. The collection of single-crystal X-ray intensity data was performed by using a CAD-4 diffractometer (Enraf-Nonius).

X-ray Analysis, Data Collection, and Refinement. $Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_5$ crystallizes in the orthorombic space group $P2_12_12$. Crystal data and diffraction information are given in Table I. X-ray intensity data of 2639 unique reflections were measured in the ω–θ scan mode; 2083, with $I \geq 2\sigma(I)$, were used for the structure determination. The experimental density was obtained by flotation in a chloroform/dibromoethane mixture. The intensity data were corrected for a decrease in intensity during data collection (22%) by using a fifth-order polynomial of the exposure time measurement, based on three different reference reflections (the number of reference points being 127). The intensity data were corrected for absorption (transmission factors varied from 0.88 to 0.95) by using a locally developed method and were reduced to structure factors.[13] The structure was solved by standard heavy-atom methods. By the use of the Ni coordinates as the starting point and Sim's weighting scheme,[14] all other atoms, including hydrogen (except H(42); see below) were located. Scattering factors were taken from ref 15. Full-matrix least-squares refinements with anisotropic temperature factors for the non-hydrogen atoms and fixed *B* values for the hydrogen atoms (7.0 Å^2) yielded values of 0.026 and 0.033 for *R* and R_w, respectively (refinement of the enantimorph led to values of 0.038 and 0.047 for *R* and R_w, respectively). Two different positions were found for the oxygen atom of one of the water molecules (O(3A) and O(3B); for the corresponding hydrogens only one position was found). The position of one hydrogen atom (H(42), attached to O(4)) appears to be disordered as well. In the final difference Fourier map about six peaks could be attributed to H(42). However, refinement of six positions for one hydrogen atom was not considered sensible. The positional parameters of the non-hydrogen atoms are listed in Table II. Anisotropic thermal parameters and hydrogen parameters are available as supplementary material,[16] as is a list of observed and calculated structure factors.

Table II. Positional Parameters for $Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_5$ ($\times 10^4$)^a

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ni	1352.9 (6)	2147.4 (5)	−2118.3 (6)
O(111)	2767 (4)	1577 (2)	−3840 (3)
O(112)	2626 (4)	719 (2)	−6083 (3)
O(12)	−491 (4)	1211 (2)	−3296 (3)
O(211)	−283 (4)	2527 (2)	−473 (3)
O(212)	3292 (4)	3263 (3)	−1459 (3)
O(22)	1675 (4)	615 (3)	−781 (3)
O(3A)^b	525 (7)	3746 (5)	−2794 (8)
O(3B)^b	826 (8)	3529 (5)	−3710 (7)
O(4)	1151 (4)	3771 (3)	2937 (4)
O(5)	0 (0)	5000 (0)	−61 (5)
C(11)	1978 (5)	1023 (3)	−4874 (5)
C(12)	101 (6)	697 (4)	−4652 (4)
C(21)	−574 (6)	1702 (4)	482 (5)
C(22)	549 (6)	575 (4)	476 (4)

^{a} Uncertainties in the last digit are indicated in parentheses. ^{b} Each 50% occupied.

Results and Discussion

Description of the Molecular Structure. The smallest structural subunit appears to be the dimeric entity $Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_2$. This unit is depicted in Figure 1, together with the atomic labeling used. The lattice water oxygens; O(4) and O(5), have been omitted for clarity. Each Ni^{2+} ion is coordinated by two halves of two different tartrate dianions, via chelation through the alcohol and the carboxylate groups. The octahedral geometry around each nickel ion is completed by a water molecule, O(3), and a nonchelating carboxylate oxygen atom of another dimer. A 2-fold axis runs through each dimeric unit and passes the centers of the central C–C bonds of both tartrates as well as water molecules, O(5), in the lattice. Important bond lengths and angles are given in Table III. Other bonding information is given in supplementary Table D.[16] Only one position (B) of the disordered, coordinated water molecule, O(3), is shown in this picture.

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(11) Yasumori, I. *Pure Appl. Chem.* **1978**, *50*, 971.

(12) Bridle, C.; Lomer, T. R. *Acta Crystallogr.* **1965**, *19*, 483.

(13) de, Graaff R. A. G. *Acta Crystallogr., Sect. A* **1973**, *A29*, 298.

(14) Sim, G. A. *Acta Crystallogr.* **1960**, *13*, 511.

(15) "International Table for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(16) See paragraph at end of paper regarding supplementary material.

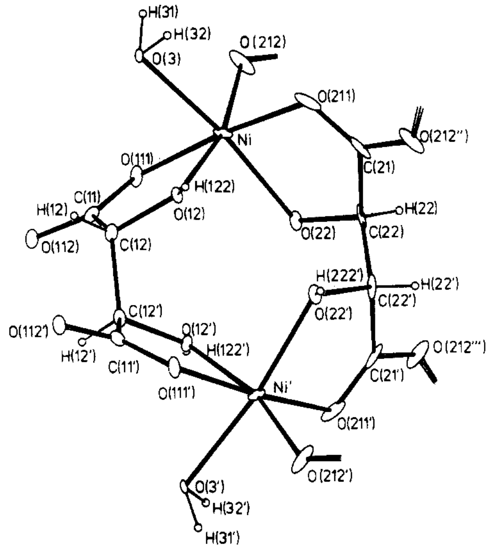

Figure 1. ORTEP drawing and atomic labeling system for a dimeric unit of $Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_2$. Noncoordinating water molecules have been omitted. Numbered atoms and equally numbered atoms bearing an accent are C_{2v} symmetry related, as are O(212'') and O(212'''). Only the B position of the coordinated disordered water molecules is depicted (see text).

Table III. Relevant Bond Lengths (Å) and Angles (deg) of $Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_5$, concerning the Coordination Sphere of Ni(II)[a]

Ni-O(111)	2.001 (3)	Ni-O(3A)	1.979 (5)
Ni-O(12)	2.065 (3)	Ni-O(3B)	2.133 (6)
Ni-O(211)	1.997 (3)		
Ni-O(22)	2.093 (3)	Ni-O(212)	2.042 (3)
O(111)-Ni-O(12)	80.3 (1)	O(211)-Ni-O(22)	79.9 (1)
O(111)-Ni-O(211)	171.9 (1)	O(3A)-Ni-O(22)	160.0 (2)
O(12)-Ni-O(212)	165.7 (1)	O(3B)-Ni-O(22)	171.2 (2)
O(111)-Ni-O(212)	90.3 (1)	O(12)-Ni-O(211)	92.2 (1)
O(22)	96.9 (1)	O(22)	88.3 (1)
O(3A)	103.0 (3)	O(3A)	93.7 (2)
O(3B)	79.4 (2)	O(3B)	83.3 (2)
O(211)-Ni-O(212)	97.7 (2)	O(211)-Ni-O(22)	103.6 (1)
O(3A)	80.2 (3)	O(3A)	77.9 (2)
O(3B)	102.8 (2)	O(3B)	84.5 (2)

[a] Other bond information is given in Table D of the supplementary material.

Possibly, disorder in the position of O(3) influences the position of tartrate group 2, since the atoms of this group show marked thermal anisotropy. Refinement using two different positions for the atoms of this group is impossible since the effect is too small. Bond lengths and angles for each tartrate ligand are normal (and do not deviate significantly from other reported tartrate coordination compounds).[17] The chelate rings (-Ni-OCCO-) are all almost planar, the maximum deviation from a least-squares best plane being 0.058 Å. The angle between the two cis chelate rings around each nickel is 87.3°, and the geometry is found to be Δ, with trans orientation of the carboxylate groups.[18] This geometry was proposed earlier on the basis of molecular model studies[8] and has also been found for other octahedrally coordinated copper(II) (*R*,*R*)-tartrate and chromium(III) (*R*,*R*)-tartrate species.[18] The coordination around nickel is distorted octahedral. The distortion is partly caused by the chelating five-membered rings and partly by the coordinated water molecule. The deviations from octahedral coordination, however, further illustrated by the Ni-O distances and O-Ni-O angles (Table III), are not so large that a different geometry should be considered. Moreover, the ligand field spectrum (vide infra) agrees with octahedral geometry. The effect of the disorder in the coordinated water positions will be discussed in more detail below.

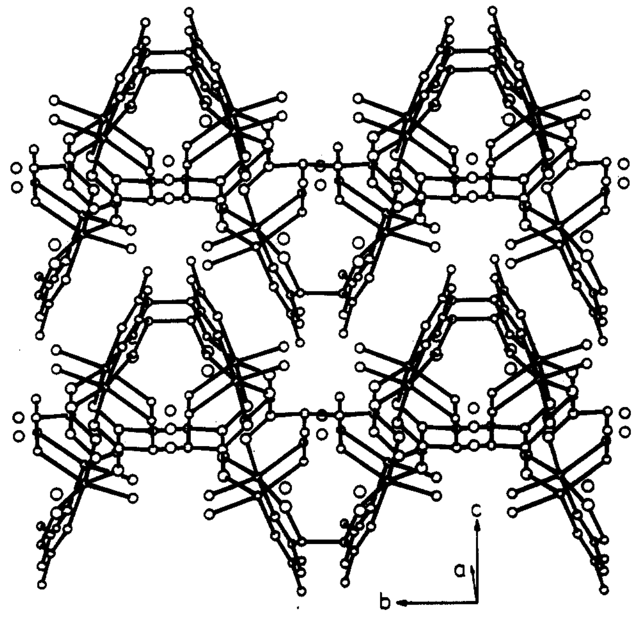

Figure 2. Projection of the crystal structure of $[Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_2](H_2O)_3$ along the *a* axis. Hydrogen atoms have been omitted for clarity. In all dimers the A position of O(3) has been used rather than the B position (see text).

Description of the Crystal Structure. The crystal of the title compound can be considered as consisting of polymeric corrugated sheets of dimeric units of $Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_2$ (described above) and water molecules (O(4) and O(5)). Within each sheet the dimers are linked together through Ni-O(212) bonds and hydrogen-bond interactions between alcohol and carboxylate oxygens of different dimers and the noncoordinated water molecules positioned between them. Between the sheets the interaction is only of hydrogen-bonding nature (in addition to van der Waals contacts), i.e. between O(3) and O(112). Figure 2 shows the packing of the dimers in the polymeric sheets and the way in which these corrugated sheets are positioned on top of one another. For the sake of clarity, hydrogen atoms are omitted and only one of the two positions found, A, for the water molecule coordinated to nickel, O(3), has been drawn. Relevant hydrogen-bond contacts (O···O varies from 2.64 to 3.03 Å) and angles are summarized in supplementary Table E.[16] The remaining feature that needs to be discussed is the disorder of the water molecule, O(3), and its effect on the crystal packing. First of all, it is to be noted that the symmetry-related contact O(3A)···O(3A), as shown in Figure 2, is only 2.89 Å, i.e. too short for a van der Waals contact (there are no hydrogen atoms present between these atoms). However, if the O(3A)···O(3B) distance (3.30 Å) is considered, this is much closer to van der Waals contacts. The cause of the disorder might therefore be that position O(3A) has a favorable hydrogen-bonding pattern whereas position O(3B) has a more favorable location in the lattice. A secondary effect of this disorder might be a small displacement of tartrate 2 (vide supra). A further effect could be the uncertainty of the hydrogen position bound to O(4). This has not been investigated in further detail.

Comparison with Dinuclear Copper(II) (*R*,*R*)-Tartrate. A more detailed comparison between the nonisomorphous structures of nickel(II) (*R*,*R*)-tartrate and copper(II) (*R*,*R*)-tartrate is now possible.[7c] Both structures contain distorted octahedrally coordinated metal ions, two distinguishable groups

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(17) Tapscott, R. E. *Transition Met. Chem. (N.Y.)* **1982**, *8*, 253.

(18) (a) Tapscott, R. E. *Inorg. Chim. Acta* **1974**, *10*, 183. (b) Ortega, R. B.; Tapscott, R. E.; Campana, C. F. *Inorg. Chem.* **1982**, *21*, 2517.

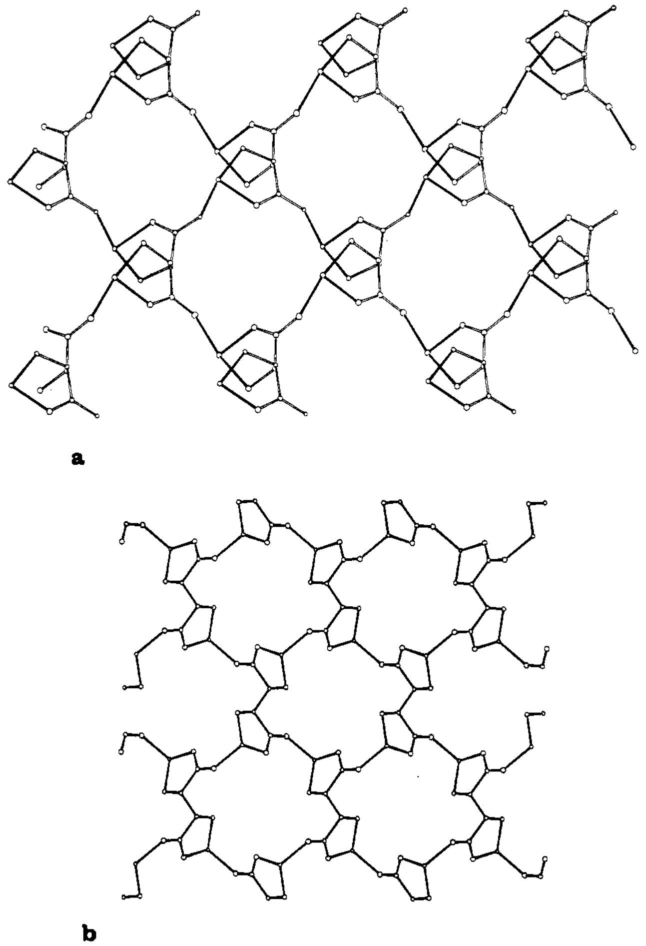

Figure 3. Binding schemes within polymeric layers of (a) copper(II) (*R*,*R*)-tartrate and (b) nickel(II) (*R*,*R*)-tartrate. Water molecules, hydrogen atoms, and tartrate groups that do not establish bonds between the dimers (other than hydrogen bridges) have been omitted.

of tartrate ligands, nearly planar cis chelate rings, dimeric entities as building blocks for the structure (with a Cu···Cu distance of 5.43 Å in a dimer, compared to Ni···Ni of 5.202 Å), and polymeric two-dimensional sheets that are held together by mere hydrogen-bond interactions. A remarkable difference, apart from the Jahn-Teller deformation of the CuO_6 octahedron (four Cu–O distances of 1.89–2.01 Å and two of 2.37–2.43 Å were found around each Cu^{2+} ion),[7c] is the fact that even the coordination of the Cu^{2+} ions by the oxygen donor ligands differs from that of the Ni^{2+} ions depicted in Figure 1. In the copper compound the coordinating water is in the trans position of the alcohol oxygen of tartrate 1 and the nonchelating carboxyl oxygen is trans coordinated to the alcohol oxygen of tartrate 2. The binding schemes of the dimeric units within the polymeric sheets are different in both compounds as well. The binding within the sheets, established by the metal ions and the tartrate 2 groups, is schematically depicted in Figure 3 (hydrogen atoms, water molecules, and tartrate 1 groups have been omitted for clarity). By the use of molecular models it can be shown that for copper the tartrate 1 groups can be located in the exposed places in Figure 3, whereas for nickel the tartrate 1 groups must be placed alternatingly above and beneath the plane of the drawing (cf. Figure 2). As a consequence, the sheets of nickel(II) *R*,*R*)-tartrate are much more corrugated than those of copper(II) (*R*,*R*)-tartrate.

Spectroscopic Measurements. The irregular coordination geometry around Ni(II) and the interesting hydrogen-bonding pattern made it worthwhile to study the compound's ligand field and IR spectra. The diffuse-reflectance spectrum of the title compound shows clear band maxima at 8900, 14400, and 25600 cm^{-1}. These three bands are typical for octahedral Ni^{2+} (NiO_6 chromophore).[19] The bands are somewhat broader than is usual for octahedral NiO_6 species.[19] This might be due to the deviations from O_h symmetry. The infrared spectra of $Ni_2((R,R)\text{-}C_4H_4O_6)_2(H_2O)_5$ show bands that can be assigned to the tartrate dianions, e.g. those at 1600 (s, br) and 1385 (s, br) cm^{-1}, for which the positions fall in the range observed earlier for other tartrate coordination compounds,[10] and water molecules. A calculation of values for ν_{OH} stretch frequencies, according to Bellamy and Owen,[20] using the O···O distances measured at −162 °C show that the (at 20 °C) observed bands in the ν_{OH} stretch region, at 3605 (w), 3465 (w), 3350 (w), 3190 (vw), 3000 (vw), and 2590 (w) cm^{-1}, do fall in the range expected for these O···O hydrogen-bond contacts.

Concluding Remarks

The results described above have first of all shown that the crystal and molecular structure of hydrated nickel(II) (*R*,*R*)-tartrate closely resembles the structure assumed in previous catalytic studies. The dimeric units with chelating tartrate dianions and two available labile coordination sites for each nickel ion, in combination with the weak contacts within and between the dimeric units, perfectly fit with the proposed mechanistic steps in the asymmetric hydrogenation of keto esters. Future work will deal with a detailed study of this mechanism, based on the present X-ray structure.

Acknowledgment. The help of Mr. S. Gorter with the X-ray diffraction measurements is gratefully acknowledged. Dr. J. A. Ibers (Northwestern University, Evanston, IL) is thanked for helpful suggestions.

Registry No. $Ni_2((R,R)\text{-}(+)\text{-}C_4H_4O_6)_2(H_2O)_5$, 90195-82-7.

Supplementary Material Available: Tables of anisotropic temperature factors of non-hydrogen atoms, positional parameters and isotropic temperature factors of hydrogen atoms, observed and calculated structure factors, bond lengths and angles, and hydrogen bond information (10 pages). Ordering information is given on any current masthead page.

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(19) Reedijk, J.; van Leeuwen, P. W. N. M.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 129.
(20) Bellamy. L. J.; Owen, A. J. *Spectrochim. Acta, Part A* **1969**, *25A*, 329.