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Crystal and Molecular Structure, Spectroscopy, and Magnetism of Diaquobis(imidazole)-*catena*-μ-(squarato-1,3)-nickel(II). A One-Dimensional Polymer

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The crystal and molecular structure of diaquobis(imidazole)-*catena*-μ-(squarato-1,3)-nickel(II), $NiC_4O_4(C_3N_2H_4)_2(H_2O)_2$, has been determined by a single-crystal X-ray analysis using three-dimensional diffractometer data. The compound crystallizes in the monoclinic system, with two formula units in a centrosymmetric unit cell, with space group $P2_1/c$ and lattice parameters a = 7.478 (1) Å, b = 11.539 (2) Å, c = 8.101 (2) Å, and β = 109.27 (2)°. The structure was solved with a direct method. A refinement by full-matrix least-squares procedures converged to $R_F = 0.023$ and $R_{wF} = 0.032$ for 1576 independent observed reflections. The Ni(II) ions are octahedrally surrounded by four oxygens of two water molecules and two squarato anions and two nitrogens of the imidazole ligands. The crystal structure contains chains of (squarato-1,3)-bridged Ni(II) ions. These chains are held together by strong hydrogen bonds between the noncoordinating oxygens of the squarato anions and the water molecules, forming a two-dimensional sheet of Ni(II) ions. These sheets are held together by weaker hydrogen bonds between the imidazole hydrogens and coordinating squarato oxygens. The Ni–N bond length (2.076 (1) Å) and Ni–O_w bond length (2.069 (1) Å) are normal. The Ni–O_s bond length (2.121 (1) Å) is rather long compared with that of similar compounds. Infrared, far-infrared, Raman, and ligand-field spectroscopies all agree with the observed crystal structure. The magnetic susceptibility data in the temperature region 1.2–100 K could best be described by neglecting the influence of the exchange coupling, yielding a zero-field splitting parameter D and $\bar{g}$ value of +5.8 (2) cm^{-1} and 2.28 (3), respectively. Fitting of the data with the available theory for Heisenberg one-dimensional coupled $S = 1$ ions, with both D and $J \neq 0$, yielded poor results.

Introduction

In magnetochemistry there is a still increasing interest for new types of bridging ligands, in order to obtain further insights into the mechanisms of the phenomenon of superexchange interactions between paramagnetic ions. A recent review on magnetically investigated transition-metal chain compounds was published by Carlin and van Duyneveldt.[1]

Recently, the magnetism and spectroscopy of a series of oxalato-bridged coordination compounds built up by chemical chains were studied.[2] Very recently, an X-ray structure investigation of one compound within this series evidenced an earlier proposed chain structure.[3] The magnetic superexchange interactions via the oxalato anions appeared to be quite large, i.e., in the order of about −10 cm^{-1}. Dimeric oxalato-bridged compounds have been investigated thoroughly and interactions of similar magnitude were found.[4] Within the dimeric compounds it is known that the magnetic superexchange interactions are strongly reduced by substitution of the oxalato ions by squarato ions.[4] One of the aims of the present investigation is to obtain a squarato-bridged chain compound and find out what happens with the superexchange interactions. To explain the value of the exchange constant, J value, in terms of the structure, we have undertaken a structural and spectroscopic study of $NiSq(IzH)_2(H_2O)_2$ (NISIA), where Sq is the squarato dianion and IzH is imidazole.

Experimental Section

IR, far-IR, Raman, and ligand-field spectra were recorded and magnetic susceptibility measurements (4.2–100 K) were performed as described elsewhere.[2] Ac susceptibility measurements in the temperature region 1.2–4.2 K were performed at a frequency of 663 Hz with a mutual inductance detector described in detail elsewhere.[5] Transparent blue-green crystals of NISIA were slowly grown from a mixture of a solution of $NiCl_2$ in water (0.01 mol/L), a solution of $H_2C_4O_4$ in water (0.01 mol/L), and a solution of $C_3N_2H_4$ (imidazole) in water (0.02 mol/L).

A specimen showing sharp optical extinctions under crossed polarizers was mounted along the c axis. On the basis of the observed extinctions ($0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$) on the spectrometer, the crystal was found to belong to the monoclinic system, space group $P2_1/c$.

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Table I. Experimental Data for X-ray Diffraction Study of $Ni(C_4O_4)(C_3N_2H_4)_2(H_2O)_2$

A. Crystal Data[a]

crystal system: monoclinic
space group: $P2_1/c$ (C_{2h}^5; No. 14)
$a = 7.478$ (1) Å
$b = 11.539$ (2) Å
$c = 8.101$ (2) Å
$\beta = 109.27$ (2)°
μ(Mo Kα) = 15.05 cm^{-1}

$V = 659.9$ Å^3
T = room temp
$Z = 2$
mol wt 343.0
ρ(obsd) = 1.7 g/cm^3
ρ(calcd) = 1.726 g/cm^3
$F(000) = 352$ electrons

B. Intensity Data

radiation: Mo Kα (λ 0.710 69 Å)
monochromator: graphite; $2\theta_{mono} = 12.8°$
reflections measd: $+h$, $+k$, $\pm l$
max 2θ measd: 60°
scan type: coupled θ(crystal)–2θ(counter)
scan range: $\Delta\theta = 0.60 + 0.35 \tan\theta$
bgd: additional scan over $\Delta\theta/4°$ on both sides of the main scan
scan speed: variable, with parameters $T_{max} = 120$ s and $\sigma(I)/I = 0.01$ calculated from a prescan[6]
horiz aperture: 4 mm; crystal to aperture, 173 mm
vert aperture: 4 mm
standard reflections: 230, 340, 151, monitored every 30 min of X-ray exposure time (variations within 3% from mean), with no decay during data collection
data set information: 2239 incl standard and extinction reflections

C. Data Reduction

absorption correction: Gaussian grid 8 × 8 × 8; min and max correction, 1.34 and 1.44
reduced reflection set: 1708 of which 132 had $I < 2.5\sigma(I)$

[a] Accurate values of the unit cell parameters and the crystal orientation matrix were determined at ambient temperature from a least-squares treatment of the angular settings of 16 reflections, carefully centered on an Enraf-Nonius CAD 4 computer-controlled diffractometer by using Mo Kα radiation (λ 0.710 69 Å).[6] The standard deviations in the lattice parameters were obtained from the comparison of the deviations from integer values of the indexes, calculated with the orientational matrix, for the angular settings of the orientation reflections as described by Duisenberg.[7]

The density calculated for two molecules in the unit cell agrees well with the value obtained by the flotation method.

Experimental data are tabulated in Table I.

The crystal selected for data collection was a parallelepiped with two additional small facets. The observed crystallographic forms, indexed in accordance with the unit cell determined by X-ray diffraction, were {100}, {010}, {001}, and {10$\bar{2}$}. Dimensions were measured under a binocular microscope and were as follows: (100)–($\bar{1}$00) = 0.22 mm, (010)–(0$\bar{1}$0) = 0.25 mm, (001)–(00$\bar{1}$) = 0.30 mm, (10$\bar{2}$)–($\bar{1}$02) = 0.34 mm. The crystal volume amounted to 1.64 × 10^{-2} mm^3.

Intensity data were collected with a CAD 4 diffractometer equipped with a scintillation counter and a PDP 8 computer. The net intensity was calculated with

$$I(\text{net}) = (\text{scale})(S - 2(L + R))/\text{npi}$$

where $L + R$ is the total background count, S the scan count, npi the ratio of the maximum possible scan speed to the applied scan speed, and (scale) a function of the time slowly varying around the value 1. To account for short- and long-range fluctuations in the intensity, the data were scaled, by interpolation in a polynomial of the third degree through eight neighboring measurement values of the standard reflection, in order to smooth out very short-term fluctuations in the intensity of the standard reflection. The standard deviation in the net intensity was calculated with

$$\sigma(I) = \frac{\text{scale}}{\text{npi}}(S + 4(L + R))^{1/2}$$

The equivalent reflections were averaged by using

$$\bar{I} = \sum_i (I_i/\sigma_i^2) / \sum_i (1/\sigma_i^2)$$

$$\sigma(\bar{I}) = \{1/\sum_i (1/\sigma_i^2)\}^{1/2}$$

where I_i and σ_i are the intensity and the standard deviation of the ith equivalent diffraction. The resulting unique set contained 1708 reflections of which 1576 had intensities above background ($I > 2.5\sigma(I)$). The data were corrected for Lorentz and polarization factors (Lp). The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F)$ by

$$\sigma(F) = \{(I + \sigma(I))/Lp\}^{1/2} - (I/Lp)^{1/2}$$

Table II. Final Positional Parameters for NISIA

atom	x/a	y/b	z/c
Ni	0.0000	0.0000	0.5000
N(1)	−0.2420 (2)	−0.0996 (1)	0.4587 (2)
N(2)	−0.5430 (2)	−0.1455 (1)	0.3879 (2)
O(1)	0.1500 (2)	−0.1619 (1)	−0.0513 (1)
O(2)	0.0492 (2)	−0.0692 (1)	0.2763 (1)
O(3)	−0.1714 (2)	0.1348 (1)	0.3699 (1)
C(1)	−0.4444 (3)	−0.2268 (2)	0.5043 (3)
C(2)	−0.2603 (3)	−0.1987 (2)	0.5466 (3)
C(3)	−0.4167 (2)	−0.0705 (2)	0.3649 (2)
C(4)	0.0679 (2)	−0.0731 (1)	−0.0243 (2)
C(5)	0.0204 (2)	−0.0296 (1)	0.1259 (2)
H(1)	−0.506 (4)	−0.280 (3)	0.539 (4)
H(2)	−0.158 (4)	−0.239 (2)	0.623 (3)
H(3)	−0.446 (4)	−0.006 (2)	0.292 (4)
H(4)	−0.662 (4)	−0.138 (2)	0.353 (3)
H(5)	−0.168 (3)	0.196 (2)	0.423 (3)
H(6)	−0.168 (3)	0.149 (2)	0.268 (3)

Solution and Refinement of the Structure

Direct methods (MULTAN 74[8]) were used to solve the structure. The positions of the nonhydrogen atoms were refined by block-diagonal least-squares procedures to $R_F = 0.055$ and $R_{wF} = 0.069$.[9] At this stage, positions of all hydrogen atoms were determined from a difference Fourier map and weights were introduced on the basis of counting statistics ($w^{-1} = \sigma(F_o^2) + 0.00002F_o^2$). Refinement was continued with a full-matrix least-squares technique. The structure refinement converged to $R_F = 0.023$ and $R_{wF} = 0.032$ for 1576 observed reflections. The positions of all atoms and the anisotropic temperature factors of the nonhydrogen atoms and isotropic temperature factors of the hydrogen atoms were refined. A total of 121 parameters including one scale factor were varied. All shifts were less than 0.2 of their standard deviations when refinement was stopped. The final positional and thermal parameters are tabulated in Tables II and III. The average deviation in an observation of unit weight, defined by $\{\sum w(|F_o| - |F_c|)^2/(m - n)\}^{1/2}$, was 3.80 as compared to the ideal value of 1. The function $\sum w(|F_o| - |F_c|)^2$ was not significantly dependent either upon F_o or upon $(\sin\theta)/\lambda$. The final R_{wF} value for all reflections including the "unobserved's" was 0.032. A final electron density difference Fourier synthesis revealed no significant residual electron density maxima higher than 0.36 e Å^{-3}. Scattering factors for all atoms were taken from Doyle,[10] except those for hydrogen which were taken from Stewart.[11] Anomalous dispersion correction for Ni was taken from a compilation by Rietveld.[12] All computer calculations were performed on a CDC CYBER-73 computer at the computer center of the University of Utrecht. Programs used in this structural analysis included the local programs CAD 4 TAPE (for handling of the diffractometer output, by D. Kaas), ASYM (averaging to the unique data set, by A. L. Spek), MULTAN 74 (the direct methods procedure of ref 8), ORTEP (thermal ellipsoid drawings, by Johnson[13]), and an extended version of the X-RAY SYSTEM (by Stewart et al.[14]) for most of the other calculations.

Results and Discussion

Description and Discussion of the Structure. The crystal structure of diaquobis(imidazole)-*catena*-μ-(squarato-1,3)-nickel(II) consists of chains built up by squarato-bridged Ni(II) ions. Contrary to the situation in $NiC_4O_4(H_2O)_2$,[15] where all squarato oxygens are coordinated directly to the Ni(II) ion, forming a sheet structure, the present compound has only two of the squarato oxygens coordinating directly to the Ni(II) ion, forming a chain structure. These two squarato oxygens bind directly to the Ni(II) ion, whereas the other two coordinate via the water molecules by intrachain hydrogen

Table III. Thermal Parameters (×10²) for NISIA[a]

atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ni	1.88 (2)	1.57 (1)	1.40 (1)	0.03 (1)	0.67 (1)	0.10 (1)
N(1)	2.24 (7)	2.21 (6)	2.51 (6)	−0.19 (5)	0.90 (5)	0.00 (5)
N(2)	1.98 (8)	3.62 (7)	3.81 (8)	−0.41 (6)	0.68 (6)	−0.02 (6)
O(1)	4.46 (7)	2.27 (5)	2.17 (5)	1.55 (5)	1.71 (5)	0.57 (4)
O(2)	3.05 (6)	2.08 (5)	1.38 (4)	0.51 (4)	0.90 (4)	0.30 (3)
O(3)	2.77 (6)	1.84 (5)	1.73 (4)	0.35 (4)	0.89 (4)	0.16 (4)
C(1)	3.08 (11)	3.60 (10)	5.36 (12)	−0.65 (8)	1.46 (9)	1.17 (8)
C(2)	2.64 (10)	3.06 (8)	4.72 (10)	−0.09 (7)	1.08 (8)	1.34 (4)
C(3)	2.63 (9)	2.82 (7)	2.84 (7)	−0.15 (6)	0.55 (6)	0.12 (6)
C(4)	2.43 (8)	1.92 (6)	1.47 (5)	0.40 (5)	0.82 (5)	0.24 (4)
C(5)	2.09 (8)	1.66 (5)	1.56 (6)	0.26 (5)	0.71 (5)	0.10 (4)
H(1)	4.3 (9)[b]					
H(2)	1.3 (5)[b]					
H(3)	2.0 (7)[b]					
H(4)	1.7 (6)[b]					
H(5)	1.5 (6)[b]					
H(6)	1.3 (4)[b]					

[a] The anisotropic thermal parameters are in the form $t = \exp\{-2\pi^2\Sigma_i\Sigma_j u_{ij}h_ih_ja_i^*a_j^*\}$ [b] Isotropic U, in Å².

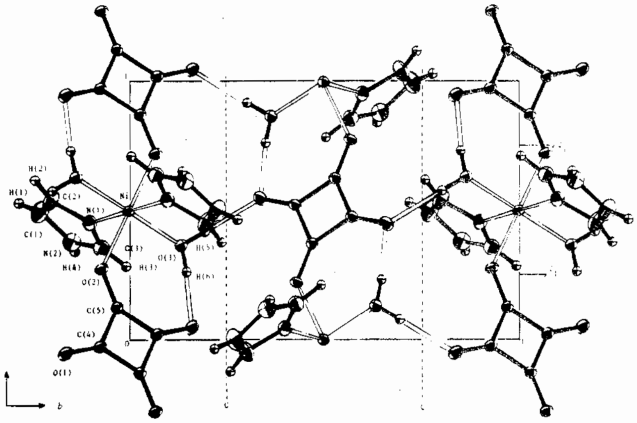

Figure 1. ORTEP drawing scaled to include 40% probability of NISIA viewed along the *a* axis.

bonds. The water molecules are coordinated directly to nickel, and the octahedron around nickel is completed by the imidazole ligands. The adopted atomic numbering scheme along with the thermal vibrational ellipsoids[13] is shown in Figure 1. A stereographic figure of the molecule is depicted in Figure 2. Interatomic bond distances and bond angles are given in Table IV. As shown clearly in Figure 1, the chains of Ni(II) ions are held together by strong hydrogen bridges between the water molecules and the coordinating squarato oxygens, thus forming a two-dimensional array of Ni(II) ions. These planes are held together by hydrogen bonds between the imidazole hydrogens and the noncoordinating squarato oxygens. The Ni–O_w bond length (2.069 (1) Å) is very similar to the one

Table IV. Interatomic Distances (Å) and Angles (deg) for NISIA

Distances

Ni–N(1)	2.076 (1)	C(1)–H(1)	0.87 (4)
Ni–O(2)	2.121 (1)	C(2)–H(2)	0.93 (2)
Ni–O(3)	2.069 (1)	C(3)–H(3)	0.93 (3)
		N(2)–H(4)	0.84 (3)
C(1)–N(2)	1.362 (3)	O(3)–H(5)	0.82 (2)
C(1)–C(2)	1.344 (3)	O(3)–H(6)	0.85 (3)
C(2)–N(1)	1.377 (2)	O(2)–H(4)[b]	2.19 (3)
C(3)–N(1)	1.320 (2)	O(1)[a]–H(6)	1.81 (3)
C(3)–N(2)	1.339 (3)	O(1)[c]–H(5)	1.93 (2)
C(4)–C(5)	1.463 (2)	O(2)–N(2)	3.012 (3)
C(4)–C(5)[a]	1.470 (2)	O(1)[a]–O(3)	2.657 (3)
C(4)–O(1)	1.250 (2)	O(1)[c]–O(3)	2.745 (3)
C(5)–O(2)	1.252 (2)		

Angles

O(2)–Ni–O(3)	95.78 (4)	Ni–O(3)–H(5)	118 (2)
O(2)–Ni–N(1)	92.37 (5)	Ni–O(3)–H(6)	115 (2)
O(3)–Ni–N(1)	88.49 (5)	H(5)–O(3)–H(6)	110 (2)
Ni–N(1)–C(2)	127.3 (1)	N(1)–C(2)–H(2)	124 (2)
Ni–N(1)–C(3)	126.6 (1)	C(1)–C(2)–H(2)	126 (2)
Ni–O(2)–C(5)	132.2 (2)	C(2)–C(1)–H(1)	134 (2)
C(1)–C(2)–N(1)	109.7 (2)	N(2)–C(1)–H(1)	119 (2)
C(2)–N(1)–C(3)	105.1 (1)	C(1)–N(2)–H(4)	125 (2)
N(1)–C(3)–N(2)	111.4 (1)	C(3)–N(2)–H(4)	127 (2)
C(1)–N(2)–C(3)	107.2 (2)	N(2)–C(3)–H(3)	125 (2)
C(2)–C(1)–N(2)	106.6 (2)	N(1)–C(3)–H(3)	124 (2)
O(1)–C(4)–C(5)	133.9 (1)	C(4)[a]–O(1)[a]···H(6)	131 (2)
O(1)–C(4)–C(5)[a]	136.0 (1)	C(4)[c]–O(1)[c]···H(5)	123 (2)
O(2)–C(5)–C(4)	132.3 (1)	C(5)–O(2)···H(4)[b]	104 (2)
O(2)–C(5)–C(4)[a]	137.8 (2)	O(1)[a]···H(6)–O(3)	174 (4)
C(4)–C(5)–C(4)[a]	89.9 (1)	O(1)[c]···H(5)–O(3)	180 (4)
C(5)–C(4)–C(5)[a]	90.1 (1)	O(2)···H(4)–N(2)	166 (4)

[a] Symmetry operation: $-x, -y, -z$. [b] Symmetry operation: $1 + x, y, z$. [c] Symmetry operation: $-x, y + {}^1/_2, {}^1/_2 - z$.

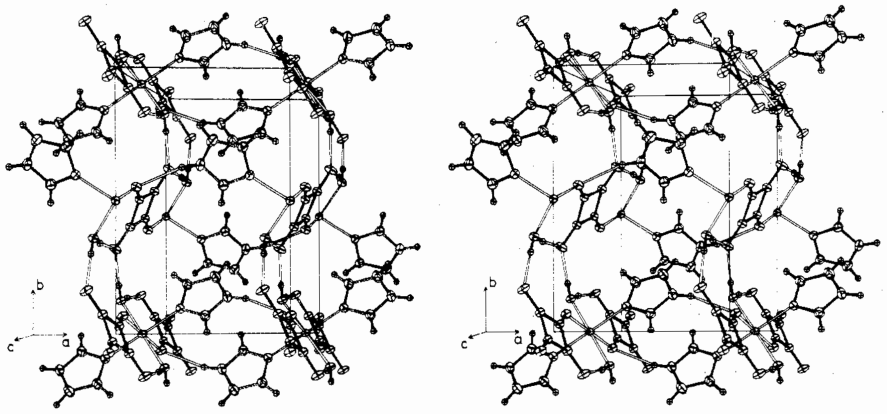

Figure 2. Stereographic drawing of NISIA.

Table V. Squarato Absorptions (cm^{-1}) in the IR and Raman Spectra of NISIA, together with the Assignment Based on D_{4h} Symmetry[a]

assignment	Raman	IR
ν_1: C-O str	1799 w (1794 w)	
ν_2: ring breathing	730 s (723 s)	
ν_3: inactive		
ν_4: out-of-plane C-O bending		243 s[c] (259 s)
ν_5: C-C str	1135 s (1123 vs)	
ν_6: in-plane C-O bending	335 w (294 w)	
ν_7: inactive		
ν_8: inactive		
ν_9: C-O str	1595 m[b] (1593 s)	
ν_{10}: ring bending	655 s (647 s)	
ν_{11}: out-of-plane C-O bending	665 w (662 w)	
ν_{12}: C-O str		1480 br (1530 br)
ν_{13}: C-C str		1100 s (1090 s)
ν_{14}: in-plane C-O bending		342 m (350 m)
$2\nu_2$: overtone	1450 w	
$2\nu_{10}$: overtone	1300 w	

[a] The results for $K_2C_4O_4$ are in parentheses. The esd is 3 cm^{-1}. [b] Slightly split band. [c] Tentative assignment, because in this region Ni-O and Ni-L bending vibrations occur.

observed for the compound $NiC_4O_4(H_2O)_2$,[15] i.e., 2.060 (9) Å. The Ni-O_s bond length (2.121 (1) Å), however, is much longer compared with the 2.085 (16) Å length in the compound $NiC_4O_4(H_2O)_2$. Presumably the two strongly coordinated imidazole ligands are responsible for the larger Ni-O_s distance. The Ni-N bond length is within the range of values reported for Ni-N distances. Angles that coordinated atoms subtend at the Ni atom are all near 90 or 180° without notable exception (see Table IV).

The squarato anion is almost square planar. The C-C bond lengths (1.463 (2) and 1.470 (2) Å) are slightly larger than the mean value found in the acid[16] (1.456 (12) Å) and close to the value reported for $NiC_4O_4(H_2O)_2$ (1.487 (16) Å). The O-C-C angles varying between 132.3 (2) and 137.8 (2)° are similar to those observed in squaric acid and $NiC_4O_4(H_2O)_2$. The C-C-C angles are very close to 90.0° (89.9 (1) and 90.1 (1)°) which deviate slightly in squaric acid (88.2 and 91.8°) and are equal to 90.0° in $NiC_4O_4(H_2O)_2$ (90.0 (1.2)°).

The nickel- and water-oxygen distances from the least-squares plane through the squarato ligand are rather small (+0.15 and −0.18 Å, respectively); therefore the chain structure is almost linear.

The geometry of the imidazole ligand is similar to that for earlier reported data[17] and will therefore not be discussed in detail here. The hydrogen bridge geometries have been included in Table IV. It is noticed that the intramolecular hydrogen bond length is slightly shorter compared to the intermolecular (interchain) hydrogen bond length (2.657 (3) and 2.745 (3) Å, respectively). The bond strength of the intramolecular hydrogen bridge is almost similar to the bond strength of the intermolecular hydrogen bridge, because of the different O---H-O angles (174 (4) and 180 (4)°, respectively). The hydrogen bond length between the imidazole nitrogen and the coordinating squarate oxygen (3.012 (3) Å) (the intersheet hydrogen bridge) and the O_s---H-N angle (166 (4)°) indicate that this latter bond strength is weak compared to the bond strength of the former hydrogen bridges. Comparison of this large distance with those observed in the chain compound $ZnOx(2MIz)_2\cdot{}^1/_2H_2O$[3] (2.78-2.80 Å) shows the present intersheet hydrogen bridge to be unexpectedly weak.

Infrared and Raman Spectra. In Table V the observed IR and Raman frequencies of the squarate molecule have been listed, together with their assignments. To assign the absorptions, we have taken the symmetry of the squarate ion as D_{4h}. The assignment is in agreement with that published by Ito et al.[18] The fact that ν_9 (a C-O stretching vibration) is slightly split and ν_6 is shifted strongly compared to the corresponding vibration in $K_2C_4O_4$[18] suggests that the symmetry of the C-O parts of the molecule is lower than D_{4h}, as evidenced by the X-ray investigation. The deviation of the low-frequency bands must also be caused by the difference in the bonding properties of potassium and nickel.

At 3250 and 3050 cm^{-1} two very broad and intense bands (having a large area of overlap) are observed. On the high-energy side a shoulder at about 3420 cm^{-1} is observed. The occurrence of these low-lying O-H and N-H stretching vibrations predicts the presence of quite strong hydrogen bridges. Bellamy and Owen[19] published an expression that related the frequency of the O-H stretching vibration and the O-O distance of the hydrogen bridge. It is calculated that for the present O-O distances (2.657 and 2.745 Å) and O-N distance (3.012 Å) the O-H and N-H stretching vibrations should occur at 3090 and 3320 cm^{-1} and at 3410 cm^{-1}, respectively; this is in nice agreement with the experimental data (vide supra).

In both the far-IR and the low-frequency part of the Raman spectrum several well-resolved absorption bands occur, i.e., the Ni-O_w, Ni-O_s, and Ni-L vibrations. The metal-oxygen vibration bands mostly are more intense compared to the metal-nitrogen vibration bands,[20] allowing a tentative assignment, based on the experience with similar oxalato-bridged coordination compounds.[2] The observed bands have been listed in Table VI. The bands at 400 and 369 cm^{-1} (IR) are assigned to the Ni-O_w and Ni-O_s stretching vibrations, respectively. Ni-O_w vibrations usually occur near 400 cm^{-1}.[20] The bands at 269 and 148 cm^{-1} are assigned to the stretching and bending vibrations of the Ni-L bond, respectively, in agreement with published data on $(Ni(imid)_6)^{2+}$ species.[21-23] In the Raman spectrum these vibrations occur at respectively 210 and 90 cm^{-1}, just as found in the nitrate compound.[21] The bending Ni-O vibrations are expected to occur below about 250 cm^{-1}, and, because in this region also squarate[18] and imidazole vibrations[21] occur, no attempts were made to assign these vibration bands. Assigning vibrations related to Ni-O bonds in the Raman spectrum gives rise to problems, because in the 300-400-cm^{-1} region the squarate molecule also has some Raman frequencies,[24] which could overlap; therefore only the observed absorption bands are listed in Table VI.

Ligand-Field Spectrum. The ligand-field spectrum of NISIA shows three strong absorptions, at respectively 1120, 627, and 376 and a shoulder at 708 nm. On the basis of ocahedral geometry, these bands are assigned to transitions from the $^3A_{2g}$

Table VI. Far-IR and Raman Frequencies of NISIA in the Region 400-50 cm^{-1}, together with Some Tentative Assignments (Esd 1 cm^{-1})

	ν_{Ni-O_W}[a]	ν_{Ni-O_S}[a]	ν_{Ni-L}[a]	ν_{Ni-L}[b]	unassigned and ligand bands
far-IR	400 vs	369 s	269 vs	148 s	342 m, 255 sh, 243 s, 217 vs, 182 m, 176 m, 126 m, 115 m, 99 w, 77 m
Raman			210 s	90 s	370 s, 335 m, 240 w, 180 w, 135 w, 105 sh, 70 m, 55 s

[a] Stretching vibration. [b] Bending vibration.

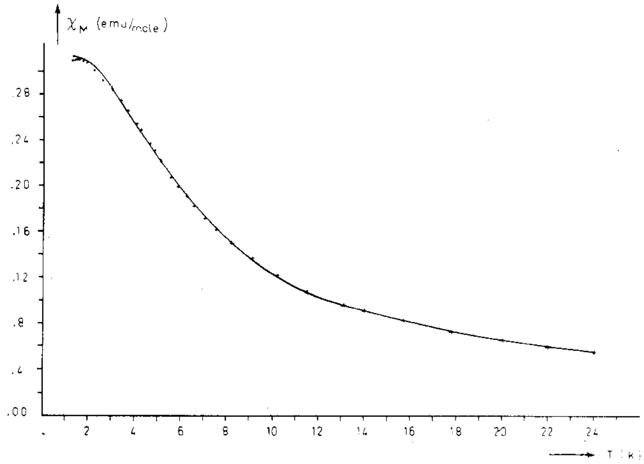

Figure 3. Molar susceptibility χ_M vs. T for NISIA. The drawn line represents the theoretical values, calculated with the susceptibility expression from ref 27, for $D = 5.8$ cm^{-1} and $g_{\|} = g_{\perp} = 2.28$.

ground state to the $^3T_{2g}$, $^3T_{1g}$ (F), $^3T_{1g}$ (P), and ^1E_g excited states, respectively. The Dq (ligand-field parameter) and B (Racah parameter) values are calculated according to published methods dealing with averaged environment.[25] Both Dq and B amount to 890 (5) cm^{-1} and are in the range normally found for octahedrally coordinated Ni(II) ions, with a ligand set of two N and four O donors.

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements at low temperatures (1.2–100 K) were carried out to see if exchange coupling between the Ni(II) ions could be observed. The magnetic moment per Ni(II) ion varies from 1.71 μ_B at 1.2 K to 3.21 μ_B at about 16 K and remains constant at higher temperatures.

The corrected[26] molar susceptibilities vs. temperature are plotted in Figure 3. In this figure also a theoretical curve expected for a monomeric Ni(II) ion with an axial zero-field splitting D is plotted. It is noticed that below 2 K the susceptibility reaches an almost constant finite value, which can be explained qualitatively in two ways. First, this behavior is consistent with the magnetism expected for a spin triplet state in an axially distorted environment,[27] with a positive zero-field splitting parameter. Secondly, this behavior can be expected for antiferromagnetically coupled Ni(II) ions; in the latter case the susceptibility should decrease again for temperatures below 1.2 K. The only way to find out if this data set implies the existence of antiferromagnetically coupled Ni(II) ions is to fit the data to theoretical susceptibility expressions obtained from one-dimensional models (vide infra).[28]

The high-temperature data (above about 10 K) obeyed the Curie–Weiss law, i.e., $\chi_M = C/(T - \Theta)$, yielding C and Θ values of 1.30 (2) emu/(K mol) and −1.1 (8) K, respectively. The calculated C value lies in the range that is normally found for octahedrally surrounded Ni(II) ions. The negative Θ value is indicative for the presence of an antiferromagnetic interaction.

Least-squares fits to the experimental values of the susceptibility expression of a spin triplet state in an axially distorted environment[27] yielded good results; however, a fit with unique spin Hamiltonian parameters D, $g_{\|}$, and $g_{\perp}$ is difficult to obtain;[29] therefore the D parameter was calculated from the very low temperature limit equation[29] (eq 1). To

$$\chi_M = 4N\beta^2 g_{\perp}{}^2/3D \qquad (kT \ll D) \qquad (1)$$

a first approximation we assumed $g_{\perp} \simeq g_{\|}$, since octahedrally surrounded Ni(II) ions generally show nearly isotropic g values.[30,31] From the high-temperature limit equation (eq 2)

$$\chi_M = 2N\beta^2\bar{g}^2/3kT \qquad (kT \gg D) \qquad (2)$$

we calculated $\bar{g} = 2.28$ (3) $\simeq g_{\perp}$. When this value for $g_{\perp}$ was substituted in eq 1, the D value was found to be +5.8 (2) cm^{-1}.

As mentioned above, the presence of a one-dimensional exchange interaction cannot be excluded; therefore, the data were also fitted to the results based on calculations on a linear-chain system (Heisenberg model). Recently, de Neef[28] published several χ vs. T curves for infinite linear chains of antiferromagnetically coupled Ni(II) ions. Fitting to these curves yields g, J, and D parameters; however, in the present case no reasonable fit could be obtained. Qualitatively, we have shown that the larger the ratio $D/|J|$, the better the fits became. Since no results are available for $D/|J| > 4$ (whose curve in fact yielded the best results), it is not possible to determine whether the model is appropriate in the present system. The only conclusion that could be drawn is that it seems as if $D \gg |J|$.

Anyway, the superexchange in the compound NISIA via the squarato anions is very much smaller than in the oxalato compounds.[2] The substitution of an oxalato bridge by a squarato bridge gives rise to very strong reductions of the superexchange interaction in chain compounds, just as observed for dimeric compounds.[4] Presumably the symmetry of the bridge orbitals affects the interaction to a great extent; it is noticed that the plane of the squarato molecule is strongly tipped away from the basal plane of the octahedron around nickel, which could result in a much smaller overlap between the π orbitals of the squarato molecule and the d orbitals of the Ni(II) ion. Furthermore, it seems that the presence of a π system in the bridging unit does not mean a priori that the superexchange will be favored.

Finally, a weak two-dimensional interchain interaction caused by the hydrogen bonds between the water molecules and adjacent squarato anions might be considered. Because of the fact that exchange via hydrogen bonds over long distances (in our case Ni···Ni = 7.1 Å) is assumed to be very weak and has only a few precedents,[32,33] this possibility was not further considered. Moreover, no theoretical models including a zero-filled splitting are known for two-dimensional $S = 1$ systems.

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Supplementary Material Available: A listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Preparation and Isomerism of Bis[μ-(trifluoromethyl)phosphido]-hexacarbonyldiiron, $Fe_2(CO)_6\{\mu\text{-}P(CF_3)(H)\}_2$. Crystal Structure of the Trans Isomer

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Reaction of $P(CF_3)H_2$ with $Fe_2(CO)_9$ gives $Fe(CO)_4\{P(CF_3)H_2\}$, pyrolysis of which produces bis{μ-(trifluoromethyl)-phosphido]-hexacarbonyldiiron, $Fe_2(CO)_6\{\mu\text{-}P(CF_3)(H)\}_2$. The phosphido-bridged dimer exists in two isomeric forms. The trans isomer crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.112$ (2) Å, $b = 8.287$ (3) Å, $c = 12.891$ (2) Å, $\alpha = 79.56$ (1)°, $\beta = 80.88$ (1)°, and $\gamma = 69.52$ (2)°. The structure has been determined from 1906 X-ray counter intensities by Patterson and Fourier techniques and refined by full-matrix least-squares methods to $R = 7.40\%$ (9.32% weighted). There is a direct interaction between the axial CF_3 group and the axial H atom, seen both in the crystal structure and in the ^{19}F NMR spectrum of a solution in CCl_3F.

Introduction

The reaction of phosphines (L) with $Fe(CO)_5$ normally results in the simple substitution of one or more carbonyl groups by L. Complexes $Fe(CO)_4L$ can also be prepared by the reaction of L with $Fe_2(CO)_9$.[2] $P(CF_3)_2H$, however, reacts with $Fe(CO)_5$ to give two phosphido-bridged species $H_2Fe_2(CO)_6\{\mu\text{-}P(CF_3)_2\}_2$ and $Fe_2(CO)_6\{\mu\text{-}P(CF_3)_2\}_2$ and with $Fe_2(CO)_9$ to give $Fe(CO)_4\{P(CF_3)_2H\}$, thermolysis of which yields the same two bridged complexes.[3]

We have investigated the reaction of $P(CF_3)H_2$ with $Fe_2(CO)_9$ and find that a simple substitution product, $Fe(CO)_4\{P(CF_3)H_2\}$, and a phosphido-bridged complex, $Fe_2(CO)_6\{\mu\text{-}P(CF_3)H\}_2$, can be prepared. The latter exists in two isomeric forms.

Experimental Section

Volatile compounds were handled in a Pyrex vacuum system. Air-sensitive solids and solutions were protected by an atmosphere of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer and calibrated against CO. Mass spectra were obtained with an AEI MS9 instrument operating at an ionizing energy of 70 eV. NMR spectra were recorded on a Brucker Spectrospin HFX machine operating at 90 MHz for ^1H and 84.66 MHz for ^{19}F nuclei. (Trifluoromethyl)phosphine, $P(CF_3)H_2$, was prepared by the literature method.[4]

Reaction of $Fe_2(CO)_9$ with $P(CF_3)H_2$. $Fe_2(CO)_9$ (0.96 mmol) and excess $P(CF_3)H_2$ (2.46 mmol) were sealed in a small tube (5 cm³). After 6 days at 21 °C, vacuum fractionation of the volatile products gave $P(CF_3)H_2$ (1.45 mmol), $Fe(CO)_5$ (0.84 mmol), and ((trifluoromethyl)phosphine)tetracarbonyliron, $Fe(CO)_4\{P(CF_3)H_2\}$ (0.61 mmol, 64%). Calcd for $C_5H_2F_3FeO_4P$: Fe, 20.7; m/e 269.8992. Found: Fe, 20.9; m/e 269.8986. The complex is an orange-brown liquid with a vapor pressure of ca. 1 mmHg at 20 °C.

Table I. Crystal Data

	isomer A	isomer B
space group	$P\bar{1}$	$P2_1/c$
a, Å	8.112 (2)	17.20 (1)
b, Å	8.287 (3)	11.41 (1)
c, Å	12.891 (2)	14.91 (2)
α, deg	79.56 (1)	
β, deg	80.88 (1)	92.57 (7)
γ, deg	69.52 (2)	
U, Å³	794.1	2924
d_{calcd}, g cm⁻³	2.02	2.19
Z	2	8
mol wt	481.7	481.7
$F(000)$	468	1872
radiation	Mo Kα	Mo Kα
λ, Å	0.710 69	0.710 69
μ, cm⁻¹	21.66	23.48

Pyrolysis of $Fe(CO)_4\{P(CF_3)H_2\}$. A pure sample (1.33 mmol) was heated to 70 °C for 7 days in a small sealed tube. The volatile products were noncondensable gas (27% H_2, 70% CO by mass spectroscopy) and small amounts (ca. 0.2 mmol each) of $P(CF_3)H_2$, $Fe(CO)_5$, and $Fe(CO)_4\{P(CF_3)H_2\}$, identified by IR and NMR spectroscopy. The residue in the tube was a red oily material, from which a lemon-colored crystalline solid, mp 92–95 °C, could be sublimed by continuous pumping at room temperature. Resublimation at 40 °C gave pure bis[μ-(trifluoromethyl)phosphido]-hexacarbonyldiiron, $Fe_2(CO)_6\{\mu\text{-}P(CF_3)H\}_2$ (0.13 mmol, 20%). Calcd for $C_8H_2F_6Fe_2O_6P_2$ m/e 481.7927; found m/e 481.7932. No other pure species could be obtained from the residue; its NMR spectrum contained no signals corresponding to hydrogen bonded directly to iron.

The ^{19}F and ^1H NMR spectra of the dimer were recorded for solutions in CCl_3F, $(CD_3)_2CO$, and CH_3CN. The IR spectrum was obtained from a solution in CH_2Cl_2. No separation of isomers was

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