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Jahn–Teller Distortion of the Electron Density in α -Nickel Sulfate Hexahydrate

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Abstract

The electron density at room temperature has been determined for α -nickel sulfate hexahydrate, α -NiSO₄·6H₂O: tetragonal, $P4_212$, $M_r = 262.86$, $a = 6.783$ (1), $c = 18.288$ (2) Å, $V = 841.4$ (3) Å³, $Z = 4$, $D_x = 2.075$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.58$ mm⁻¹, $F(000) = 544$. $R = 0.023$, $wR = 0.026$ from 1864 independent reflections using X-ray diffraction data from a previous study of its structure, absolute chirality and optical activity [Stadnicka, Glazer & Koralewski (1987). *Acta Cryst.* **B43**, 319–325]. Although the charge on the [Ni(H₂O)₆] moiety of 1.7 (2) e determined by partitioning the difference density is close to the formal value, the Ni atom carries a net negative charge of -0.46 (2) e. Contrary to expectation, only four lobes of electron density are evident in the vicinity of the Ni atom. They are aligned toward the four second nearest-neighbour S atoms. Along the Ni—S vectors the maximum $\Delta\rho$ is 1.3 e Å⁻³. There is no significant

concentration of the electron density in other directions.

Introduction

The structure consists of S—Ni layers normal to the c axis (Fig. 1). The S—Ni—S angles are 90°. Each Ni atom is coordinated to six water molecules in an octahedral configuration with each hexaaquanickel moiety linked *via* a hydrogen-bond network to the four coplanar sulfate groups shown in Fig. 2(a). These groups lie 4.8 Å from the Ni atom and two lie along a twofold axis in the [110] direction. The hexaaquanickel moiety is also connected by the hydrogen-bond network to two sulfate groups in the layers above and below the Ni atom (Fig. 3a). These sulfate groups are located 5.4 Å from the Ni. Because the geometries of the first and second nearest-neighbour interactions are distinctly different, this structure provides a means of assessing their relative importance.

McIntyre, Ptasiwicz-Bak & Olovsson (1990) in their study of $\text{NiSO}_4 \cdot 6\text{D}_2\text{O}$ found no indication of significant interactions between the Ni atom and its second coordination sphere. Their analysis was based on multipole modelling of electron density obtained from combined neutron and X-ray data.

Other recent studies have published evidence supporting the hypothesis that second nearest-neighbour interactions should be taken into account when interpreting the electron distribution around transition-metal atoms (Maslen, Ridout & Watson, 1988; Maslen, Watson & Moore, 1988; Maslen & Spadaccini, 1987). The apparent contradiction warrants further examination of the difference density for α -nickel sulfate hexahydrate.

Experimental

The data for this study were from Stadnicka, Glazer & Koralewski (1987). These intensities were corrected for Lorentz-polarization and absorption before being averaged. Experimental and the present refinement results are given in Table 1. Refinement, based on F , using the spherically averaged atomic scattering factors of Cromer & Mann (1968) and including the dispersion corrections of Cromer & Libermann (1970) resulted in the final residual factors of $R = 0.025$ and $wR = 0.032$. The refined thermal and positional parameters were within 3σ of the parameters originally reported by Stadnicka *et al.* (1987).

Although the accuracy of the original data was adequate for an analysis of the electron density, no correction had been applied for extinction. We there-

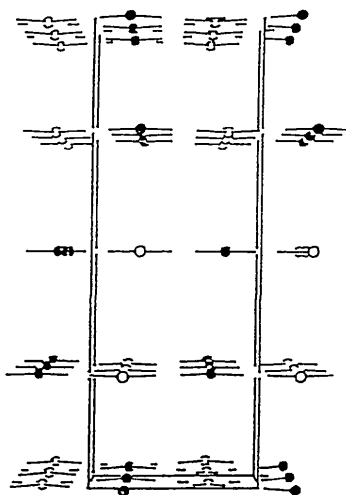


Fig. 1. Nickel sulfate unit cell showing arrangement of Ni and S atoms in layers. Filled circles represent Ni atoms, open circles S atoms.

fore refined a secondary-extinction parameter (Larson, 1970), the largest correction being 0.77 for the 004 reflection. The final R and wR were 0.023 and 0.026 respectively. Calculations were performed on a Sun 3/280 and a Decstation 5000 using the XTAL3.2 system of crystallographic programs (Hall & Stewart, 1992). The positional parameters agree well with the values obtained before application of extinction; however, several of the thermal parameters shifted significantly after the extinction

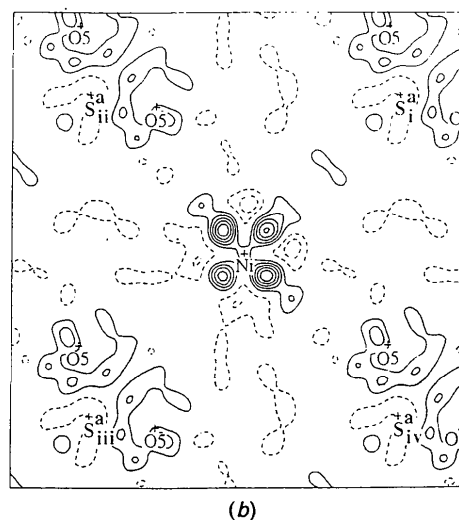
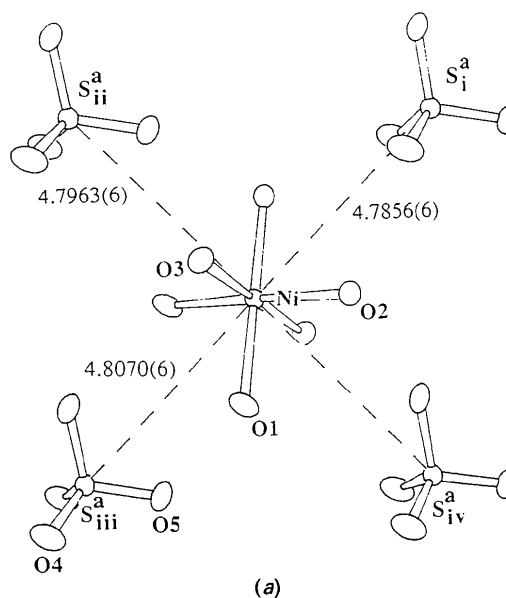


Fig. 2. (a) Arrangement of sulfate groups around the Ni coordination octahedron (H atoms have been omitted for clarity). (b) $\Delta\rho$ in a section through the Ni coordination octahedron in the plane containing the Ni-S vectors shown in (a). Border $10 \times 10 \text{ \AA}$, contour interval 0.2 e \AA^{-3} , solid contours - positive, dashed contours - negative.

refinement. The largest shift was 5σ for the Ni and S U_{11} parameters.*

Atomic charges

Atomic charges evaluated by a Hirshfeld (1977) partitioning of the difference density are listed in Table 2. The charges for the sulfate group and hexa-aquanickel moiety are about 80% of their formal

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55985 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

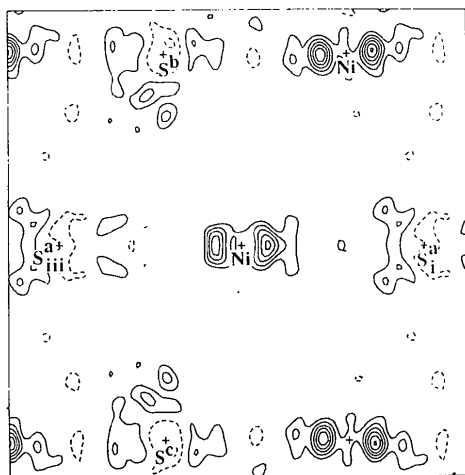
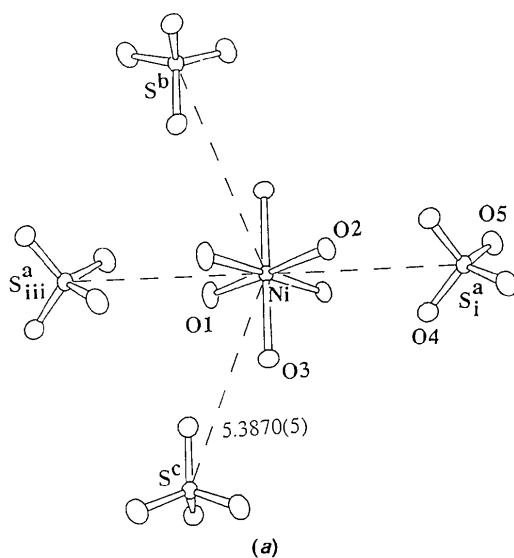


Fig. 3. (a) Relationship of Ni to sulfate groups in neighbouring layers. (b) $\Delta\rho$ in plane of (a). Border 11.8×11.8 Å, contours as in Fig. 2(b).

Table 1. *Experimental and refinement parameters*

Diffractometer	Enraf-Nonius CAD-4
Monochromator	Graphite
Scan type	$\theta-2\theta$
θ scan with ($a + b \tan \theta$) ($^\circ$)	0.75, 0.35
Number of reflections measured	4009
Transmission range in absorption corrections	0.456–0.531
R_{int}	0.027
Number of independent reflections ($0 \leq h \leq 11, 0 \leq k \leq 11, -30 \leq l \leq 30$)	1864 ($ F_{max} > \sigma$)
Maximum extinction correction	0.77
R	0.023
wR	0.026
S	3.75 (6)
Weights	$1/\sigma^2$
Final max. Δ/σ (non-H, H)	0.0029, 7.7×10^{-5}
Max. height in final difference Fourier synthesis ($e \text{ \AA}^{-3}$)	1.3
Min. height in final difference Fourier synthesis ($e \text{ \AA}^{-3}$)	-0.6

Table 2. *Atomic charges (e)*

	Charge		Charge	Hydrogen-bond length ($D-H \cdots A$) $D \cdots A$ (Å)
Ni	-0.46 (2)	H11	0.25 (1)	2.718 (2)
S	-0.25 (2)	H12	0.12 (1)	2.792 (2)
O1	0.16 (1)	H21	0.24 (1)	2.775 (2)
O2	0.01 (1)	H22	0.16 (1)	2.749 (3)
O3	0.02 (1)	H31	0.01 (1)	2.820 (2)
O4	-0.35 (1)	H32	0.12 (1)	2.729 (2)
O5	-0.38 (1)			
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	1.7 (2)			
$[\text{SO}_4]^{2-}$	-1.7 (2)			

values. All hydrogen charges are positive, and those O atoms in the chemically equivalent sets {O1, O2, O3} and {O4, O5} agree in sign and are broadly consistent in magnitude. The closer agreement for the sulfate O atoms is as expected from the similarity of the S—O4 and S—O5 bond lengths [1.475 (2) and 1.474 (1) Å respectively]. The charge on the O1 atom involved in the short Ni—O1 bond [2.013 (1) Å] is more strongly positive, in agreement with a tendency for depletion of electrons from shorter bonds noted by Maslen, Ridout & Watson (1988). There is weak correlation between the charges determined for the H atoms and the hydrogen-bond strength as indicated by the distances in Table 2.

The Ni atom carries a highly significant negative charge which at first appears to be anomalous. However, Maslen & Spadaccini (1987) report a similar negative charge of $-0.48 e$ for Ni in potassium bis(dithiooxalato- S,S')nickelate.

The Jahn–Teller theorem (Jahn & Teller, 1937) states that certain transition-metal complexes will be unstable in configurations of high symmetry, distorting to form more stable complexes of lower symmetry. Stable octahedral ligand geometries do not occur when the central atom has a d^9 ground state. Atoms with a d^8 electronic ground-state configuration, such as Ni^{2+} , do not form the Jahn–Teller-distorted structure characteristic of the d^9 configuration. $O_h \rightarrow D_{4h}$

distortion is a well documented example of removing instability by stretching the coordination octahedron along one axis of the octahedron, causing the reduction to D_{4h} symmetry.

The negative charge on the Ni atom in nickel dithiooxalate implies that the Ni atom tends towards a d^9 configuration, with the resulting Jahn–Teller distortion of the coordination octahedron favouring the square-planar configuration found in that structure. However there is, at most, a very faint suggestion of a Jahn–Teller distortion in the ligand geometry of the title compound.

Electron density

Prominent features in the difference density are confined to the (001) plane, which is parallel to a cleavage plane of the title compound. An absence of interaction between the (001) planes is suggested by the featureless electron density between the planes in Fig. 3(b) [the (001) planes are viewed edge on]. Significant interactions within the (001) plane and weak interaction between the equivalent planes is consistent with (001) cleavage.

The electron density around the Ni atom contains four coplanar lobes of electron concentration (Fig. 2b). The Ni—O1—O2 plane and the crystallographic (001) plane intersect along the [110] direction of the unit cell, the plane normals making an angle of approximately 45° . The two lobes oriented towards S_i^a and S_{iii}^a in Fig. 2(b) lie along the line of intersection. These lobes bisect the O1—Ni—O1 and the O2—Ni—O2 angles. The other two lobes are oriented toward the centres of opposite faces of the nickel coordination octahedron.

All lobes of electron concentration have peaks of 0.90 – $1.3 e \text{ \AA}^{-3}$ situated 0.6 – 0.7 \AA from the Ni nucleus. Those along the twofold axis of the cell (the [110] direction of both cell and coordination octahedron) are asymmetric, presumably due to the differing alignments of the sulfate group with respect to the Ni atom.

The lobes perpendicular to these and lying out of the Ni—O1—O2 plane have a weak double-peaked structure (Figs. 2b, 3b), with the second peak of $0.40 e \text{ \AA}^{-3}$ located 1.4 \AA from the nucleus. This double-peaked structure has been observed previously by Spadaccini (1988) in studies of the transition-metal silicate spinels which also involve non-ideal octahedral coordination of a transition metal with oxygen ligands.

The configuration of the lobes cannot be explained in terms of conventional models of coordination bonding. The $3d$ electronic states for an atom in an octahedral complex fall into two groups, e_g and t_{2g} orbitals. For nearly complete $3d$ subshells the t_{2g}

states are preferred, forming lobes of electron density oriented in all $\langle 111 \rangle$ directions of the coordination octahedron. The e_g orbitals generate lobes oriented along the $\langle 100 \rangle$ axes of the octahedron. The electronic distribution around the Ni cannot be explained in terms of electron movement into the lower energy t_{2g} orbitals in this structure, as the lobes are not aligned along all diagonal directions. Only four lobes are present instead of the eight required for an ideal t_{2g} configuration, and only two of these four lie close to the $\langle 111 \rangle$ directions of the coordination octahedron.

In addition, all lobes lie along Ni—S vectors (Fig. 2b). The plane of Fig. 2(b) is represented by the dashed lines in Fig. 2(a). Concentration of electron density along these lines is not favourable energetically, because the lobes are oriented towards the negatively charged sulfate groups. We therefore infer that the lobes are produced by exchange interaction between the Ni atom and sulfate groups. Exchange effects diminish rapidly with distance, whereas a point-charge Coulomb potential diminishes only as $1/r$, where r is the interchange separation. There is no electron density associated with the vector connecting the Ni atom to the sulfate groups in the next layers (S^b and S^c in Fig. 3b). The centres of these sulfate groups are 0.6 \AA further away than the sulfate groups shown in Fig. 2(a). As exchange interactions decrease rapidly with distance, this is consistent with generation of the lobes of density near Ni by exchange interactions.

Discussion

The electron difference density is sensitive to errors in the data collection and refinement procedure. Multipole modelling of the deformation density reduces the sensitivity to experimental errors, and affords the possibility of separating the contributions of each atom. This approach has been taken by McIntyre *et al.* (1990) in their study of the deuterated form of the title compound. That study shows how the difference density can be deconvoluted into a set of atom-centred fragments, each with approximate symmetry corresponding to that of the nearest-neighbour geometry. However, due to the overcompleteness of the set of multipole functions, modelling of the electron density with a set of multipole parameters is not unique. Care is required when interpreting individual atom difference densities based on multipole refinement of the total density. In particular, the appearance of features in an isolated-atom difference map which do not occur in the total difference density map implies cancellation between components with opposite sign arising from different isolated-atom density maps. As the physical properties determined by the difference density are related

to the sum of the components such cancellations may have a significance comparable with that of the component densities. It is not necessarily accidental for cancellation to occur along only a subset of the bonds which in terms of nearest-neighbour interactions are equivalent. Therefore the relationship between isolated-atom density maps should be examined to assess the physical validity of the electron distribution, before confirming conclusions based on the topographies of single isolated-atom density distributions.

The Ni deformation density obtained by McIntyre *et al.* (1990) appears to be physically reasonable. However, the isolated Ni-atom deformation densities contain several features not present in the total deformation density. When the validity of the Ni features is discussed, the physical significance of the cancelling density belonging to surrounding atoms is not made clear, that is, the implications of the disappearance of isolated-atom features in the total density maps are not considered. The results of McIntyre *et al.* (1990) do not justify their assertion that the Ni deformation electron density is influenced solely by the ligand geometry, as inspection of their results shows.

In Figs. 2(c) and 2(c') of McIntyre *et al.* (1990), the electron density in two positive lobes is enhanced relative to that of a second pair. The two stronger lobes have a double-peaked structure. Our section corresponding to Fig. 2(c) of McIntyre *et al.* (1990) is displayed in Fig. 4. In both our map and that of McIntyre *et al.* (1990) the electron density is distributed unevenly between orbitals. The uneven distribution is not explicable in terms of the first coordination sphere. The double-peaked lobes of our Fig. 4 and Figs. 2(c) and 2(c') of McIntyre *et al.* (1990) lie along the $S_{II}^a-Ni-S_{IV}^a$ vector.

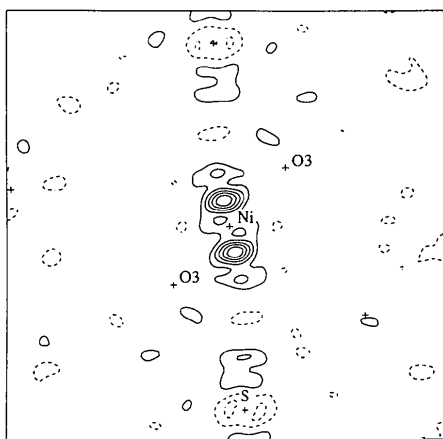


Fig. 4. $\Delta\rho$ in the plane through Ni, O3 and the internal bisector of O1 and O2. Border $11.2 \times 11.2 \text{ \AA}$, contours as in Fig. 2(b).

A similar observation applies to Figs. 2(a) and 2(a') of McIntyre *et al.* (1990). Two lobes are enhanced relative to the second pair in the map. The enhanced lobes lie along the $S_{II}^a-Ni-S_{III}^a$ vector, as inspection of our Fig. 3 indicates.

The shape of the density near the Ni atom cannot be explained in terms of the nearest-neighbour oxygen positions and the departures from ideal octahedral symmetry. The significance of interactions with second nearest-neighbour sulfate groups is indicated by the orientation of the lobes.

If we can regard the Ni atom and sulfate groups as forming a Jahn-Teller-distorted system, the relationship between the charge on the Ni atom, the structural geometry and the difference density becomes clear. Such a distortion is possible because the Ni carries a charge of about half an electron and therefore has an electronic configuration approaching d^9 . Jahn-Teller $O_h \rightarrow D_{4h}$ distortion occurs in the title compound with the axis of distortion perpendicular to the plane of the Ni-S^a vectors, leading to a square-planar coordination geometry. For strong overlap of the ligand atoms in a square-planar configuration with a d^9 ground state the electron density is depleted because of the predominance of the depletion due to overlap of electrons with parallel spins. That accounts for the well known e_g depletion of electrons in Cu-O bonds. There is far less overlap of electron density between second nearest neighbours however, and the results of this analysis indicate that concentration of ρ due to overlap of electrons with paired spins in the second nearest-neighbour e_g orbitals predominates. The lobes observed are explained as the e_g orbitals belonging to the Ni-S system, rather than as t_{2g} orbitals relating to the Ni(H₂O)₆ moiety. The two sulfate groups lying 5.3 Å from the Ni atom are displaced from ideal D_{4h} coordination positions (along the Ni-O3 vectors), by O3-O4 repulsion (Fig. 3a). The four coplanar sulfate groups avoid close O-O contacts and therefore lie closer to the Ni atom.

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A Test of the Importance of Weak Reflections in Resolving a Space-Group Ambiguity Involving the Presence or Absence of an Inversion Centre

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Abstract

The structure of margarite, $\text{CaAl}_2[\text{Al}_2\text{Si}_2\text{O}_{10}](\text{OH})_2$, has been reported in space group $C2/c$, and in the corresponding non-centrosymmetric space group Cc . Previous refinements of margarite in space group Cc were marred by strong correlations affecting parameters that are inversion related in $C2/c$. Refinement of single-crystal X-ray diffraction data, collected with synchrotron radiation, converged without large correlations in Cc . The refinement was based on 4056 F_{obs} , without merging Friedel pairs, including all the weak reflections ($R = 0.027$). No atom in Cc is removed further than 0.08 Å from its corresponding position in $C2/c$. The R in space group $C2/c$, after merging of the Friedel mates, was 0.059 (2658 F_{obs}). For the weak F_{obs} the disagreement in space group $C2/c$ is much worse than in Cc . This agrees with the warning that it is the weak F_{obs} which are most sensitive to small non-centrosymmetric distortions [Schomaker & Marsh (1979). *Acta Cryst.* **B35**, 1933–1934]. Removing weak F_{obs} from the data results in a data set resembling one that could have been collected using an X-ray tube (with omission of weak F_{obs}). In the Cc model without weak F_{obs} many of the correlation coefficients rose dramatically to values

over 0.9, and consequently difficulties occurred in converging the refinement and the estimated standard deviations increased fourfold compared to the values obtained for refinement of the full data set. Therefore, if one wishes to resolve a space-group ambiguity: (1) one should collect precise data, and especially collect as many weak reflections as precisely as possible; (2) one should include all reflections in the refinement, even if this raises the R value – a more complete data set, with a higher R value may be more important in establishing the symmetry than a smaller data set with a lower R value; (3) when measuring at a synchrotron one should use a wavelength which emphasizes the anomalous-dispersion contribution in order to make the differences between the Friedel pairs more significant.

Introduction

Space group Cc has the distinction of being erroneously assigned most often in crystal structure determinations. At least 11% of all crystal structures determined in this space group actually have a higher symmetry (Baur & Kassner, 1992). Of 35 cases reported in which the symmetry of a crystal structure described originally in space group Cc was revised

† Deceased 13 June 1990.