Molecular and Crystal Structure, and EPR Studies of Tetraphenylarsonium [Bis-(1,3-dithia-2-one-4,5-dithiolato)-nickelate], (AsPh₄)[Ni(dmid)₂]

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Crystal Structure, EPR Studies, Tetraphenylarsonium [Bis-(1,3-dithia-2-one-4,5-dithiolato)-nickelate]

The crystal structure of (AsPh₄)[Ni(dmid)₂] (dimid⁻ = 1,3-dithia-2-one-4,5-dithiolato) has been determined by X-ray diffraction studies: crystals are monoclinic, space group P2₁/n, a = 14.724(2), b = 14.305(5), c = 15.570(3) Å, β = 92.0(1)°. V = 3277 Å³, ρ₀ = 1.63 g cm⁻³ for Z = 4, final conventional agreement indices R = 0.038 and R_w = 0.049 for 2115 unique, observed reflections and 211 variable parameters. The asymmetric unit contains one (AsPh₄)⁺ cation and one [Ni(dmid)₂]⁻ anion, both in general positions. The anions are isolated from each other by the bulky cations. The [Ni(dmid)₂]⁻ ion deviates strongly from planarity: the dihedral angle between the two Ni(dmid) moieties is 10.7°; one of the dmid ligand is almost planar, while the second one is severely puckered. Polycrystalline powder and single crystal EPR spectra have been recorded at room temperature. Only one signal was observed in all crystal orientations. The angular dependences of the linewidth and of the g values have been determined, as well as the principal g values and directions. These results have been compared to those previously obtained for the analogue (n-Bu,N)[Ni(dmid)] (dimid⁻ = 1,3-dithia-2-thione-4,5-dithiolato), and discussed in terms of the localization of the unpaired electron on the ligands, leading to a formal (III) and actual (II) nickel oxidation state.

Introduction

Salts with fractional oxidation state and π donor-acceptor compounds derived from the [M(dmid)]⁻⁻ complexes (M = Ni, Pd, Pt; dmid⁻⁻ = 1,3-dithia-2-thione-4,5-dithiolato) exhibit electrical properties that are out of the ordinary [1, 6]. In particular two of such compounds, TTF[Ni(dmid)₂] [3] and (Me₆N)[Ni(dmit)₂] [5], undergo a superconducting transition under pressure. It was thus interesting to extend such investigations to other similar polysulfur-ligand complexes and we have recently shown that the oxygen-derived [M(dmid)]⁻⁻ systems (M = Ni, Cu, Pd, Pt; dmid⁻⁻ = 1,3-dithia-2-one-4,5-dithiolato; Fig.1) also are a source of conductive salts with fractional oxidation state and π donor-acceptor compounds [7, 8].

We report here the X-ray structure determination and EPR studies of the (AsPh₄)[Ni(dmid)₂] precursor complex. These results have been compared to those obtained from similar studies of the (n-Bu,N)[M(dmit)₂] sulfur-analogue complexes [9, 10].

Experimental

Synthesis and crystal growth

(AsPh₄)[Ni(dmid)₂] has been prepared as previously described [7]. Good-quality single crystals have been obtained by dissolving the brown microcrystalline raw product in a mixture of methanol: DMF (7:1) and cooling the resulting solution at −35 °C.

X-ray structure determination

Crystal data are reported in Table I together with relevant details of the intensity data collection. The intensity of three standard reflections was monitored throughout the data collection; no significant fluctuation was noticed. The usual Lorentz-polarization fac-

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Crystal data

Formula: C_{30}H_{20}AsNiO_{2}S_{8}
Crystal system: Monoclinic
a = 14.724(2) Å
b = 14.305(5) Å
c = 15.570(3) Å
β = 92.20(1)°
ρ_{exp} = 1.61(2) g cm^{-3}
ρ_{x} = 1.63 g cm^{-3}
Crystal size: 0.5×0.17×0.025 mm³
Elongation axis: [010]

Data collection
T = 293 K
Diffractometer: CAD4 Enraf-Nonius
Radiation: MoKα, λ = 0.71069 Ä, graphite monochromator
Crystal-detector distance = 207 mm
Detector window: height = 4 mm, width = 4 mm
Take-off angle = 4°
Scan mode: ω-2θ, maximum Bragg angle = 22°
Scan width = (0.8 + 0.35 tg θ)° for ω angle
Parameters determining the scan speed*
SIGPRE = 0.5 SIGMA = 0.015 VPRE = 10° min^{-1} TMAX = 90 s

Refinement
Number of reflections for the refinement of cell dimensions: 25
Number of recorded reflections: 5731 (excluding standards)
Number of utilized reflections (NO): 2115 \[I > 2\sigma(I)\]
Number of variable parameters (NV): 211

Final reliability factors
R = Σ|k|\|Fo|−|Fc||Σk|Fo| = 0.038
Rw = [Σw(k|Fo|−|Fc|)²Σw(Fo|²)]^{1/2} = 0.049
S = [Σw(k|Fo|−|Fc|)²(NO−NV)]^{1/2} = 1.44
where w = 1.35/[σ²(Fo|²) + 0.001 Fo|²]

tors were applied to the net intensities. Absorption corrections were calculated by the Gaussian integration method [11], using a 32×4×4 grid; maximum and minimum transmission coefficients were 0.951 and 0.714 respectively and the average transmission coefficient was 0.905.

The structure was solved by direct methods. Least-squares refinement was conducted using the block-diagonal approximation in the first stages and full-matrix in the final stages. Scattering factors were taken from [12] and anomalous dispersion corrections were applied to non-hydrogen atoms. Phenyl rings were treated as idealized rigid groups (C—C = 1.395 Å and C—C—C = 120.0°), with an individual isotropic temperature factor for each carbon atom and a fixed arbitrary temperature factor (U = 0.07 Å²) for hydrogen atoms. All other atoms were given anisotropic thermal parameters. Final agreement factor values figure in Table I. Positional parameters and equivalent isotropic temperature factors for non-hydrogen atoms are given in Table II; atoms are labelled according to Fig. 1. Components of the anisotropic temperature factors, hydrogen atom positional parameters, observed and calculated structure factor amplitudes, and deviations of atoms from least-squares planes and dihedral angle between planes have been deposited as supplementary material*.

Table III. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length/°</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni—S(1)</td>
<td>2.162(2)</td>
<td>0.072(5)</td>
</tr>
<tr>
<td>Ni—S(2)</td>
<td>2.143(2)</td>
<td>0.072(5)</td>
</tr>
<tr>
<td>Ni—S(3)</td>
<td>2.147(3)</td>
<td>0.072(5)</td>
</tr>
<tr>
<td>Ni—S(7)</td>
<td>2.155(2)</td>
<td>0.072(5)</td>
</tr>
<tr>
<td>S(1)—C(1)</td>
<td>1.721(8)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(2)—C(2)</td>
<td>1.715(8)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(3)—C(3)</td>
<td>1.748(8)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(4)—C(4)</td>
<td>1.738(8)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(5)—C(5)</td>
<td>1.760(9)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(6)—C(6)</td>
<td>1.760(9)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(7)—C(7)</td>
<td>1.749(9)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(8)—C(8)</td>
<td>1.750(9)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(9)—C(9)</td>
<td>1.749(9)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(10)—C(10)</td>
<td>1.750(9)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(11)—C(11)</td>
<td>1.879(4)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(12)—C(12)</td>
<td>1.887(4)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(13)—C(13)</td>
<td>1.887(4)</td>
<td>0.03(8)</td>
</tr>
<tr>
<td>S(14)—C(14)</td>
<td>1.892(4)</td>
<td>0.03(8)</td>
</tr>
</tbody>
</table>

* Lists of structure factors and anisotropic thermal parameters have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Copies may be obtained by quoting the deposition number CSD 53266, the authors, and the journal reference.
EPR spectra

EPR spectra were recorded at X- and Q-band by using a Bruker ER 2000 and a Varian EQ spectrometer, respectively.

Results and Discussion

Fig. 2 is a view of the unit cell content. The crystal structure consists of isolated [Ni(dmid)₂]⁻ anions surrounded by the bulky (AsPh₄)⁺ cations, in such a way that no close stacking is observed. The asymmetric unit contains one (AsPh₄)⁺ cation and one [Ni(dmid)₂]⁻ anion, both in general positions. The proposed stoichiometry is thus confirmed and the nickel atom could be considered to be in the formal Ni(III) oxidation state. From this point of view the title compound is analogous to (n-Bu₄N)[Ni(dmit)₂] described by Lindqvist et al. [9]. However, it will be shown later that the actual oxidation state of the nickel atom in both complexes is more probably II. The average Ni—S distances are quite consistent: 2.152 Å in [Ni(dmid)₂]⁻ and 2.156 Å in [Ni(dmit)₂]⁻; C—S and C—C distances also agree fairly well and have values intermediate between single and double bond lengths, indicating a high degree of electron delocalization. The C—O distances of 1.20 Å are close to the double-bond value as are the terminal C—S distances in [Ni(dmit)₂]⁻; as a matter of fact this comparison can be extended to all oxidized [Ni(dmit)₂]⁻ species for which detailed structural data are available [1, 2, 14]. In all these species the Ni(dmit)₂ entities are planar or fairly close to planarity; the more strongly distorted Ni(dmit)₂ group is observed in (n-Bu₄N)[Ni(dmit)₂] where the dihedral angle between the two Ni(dmit) moieties is 6.1° [9]. On the opposite, the [Ni(dmid)₂]⁻ ion in (AsPh₄)[Ni(dmid)₂] deviates strongly from planarity. Furthermore, one of the dmid ligands is almost planar, while the second one is severely puckered as illustrated in Fig. 3. The dihedral angle between the two Ni(dmid) mean planes is 10.7°. This distortion is similar to or even higher than those observed in TTF[Pt(dmit)₂]₃ [2], TTF[Pd(dmit)₂]₂ [15], or (n-Bu₄N)₁[Pd(dmit)₂] [16]: yet, in all these complexes a direct metal—metal interaction induces the formation of [M(dmit)₂]₂ dimers and thus the folding of the normally planar M(dmit)₂ units (dihedral angles are 11.2°, 6.3°, and 6.2°, respectively). In the case of (AsPh₄)[Ni(dmid)₂] there is at this point no such evident theoretical reason for such a distortion and only packing effects could be invoked to explain this unusual structural feature.

Fig. 2. Perspective view of the unit cell of (AsPh₄)[Ni(dmid)₂].
Polycrystalline powder EPR spectra of \((\text{AsPh}_4)[\text{Ni(dmid)}_2]\) at X- and Q-band frequency at room temperature are shown in Fig. 4. Single crystal spectra were recorded at X-band frequency at room temperature by rotating around the \(a^*, b\) and \(c\) axes. Only one signal was observed in all the crystal orientations: the angular dependences of the linewidth and of the \(g\) values, with the calculated best fit curve, are shown in Fig. 5. The principal \(g\) values and directions are shown in Table IV: one principal direction is along \(b\), as expected for exchange narrowed signals. The other two directions are in the \(a^*c\) plane, rotated of ~50° from the axis. The lineshape, analyzed as previously reported [17], results Lorentzian thus confirming the exchange narrowed character of the spectra.

In the monoclinic cell there are four \([\text{Ni(dmid)}_2]\)^+ chromophores, two by two related by a center of symmetry or by a reflection plus a translation. From an EPR point of view, atoms related by an inversion center are magnetically equivalent, while those related by a reflection are not, so we expect two non-equivalent sites in the cell with non parallel \(g\) tensors, i.e. tensors having the same principal values but different orientations.
Table IV. Experimental principal values and directions of the crystal g tensor for \((\text{AsPh}_4)[\text{Ni}(\text{dmit})_2]\) and calculated values of \(g_{\text{M1}}\) and \(g_{\text{M2}}\) molecular tensors, assuming the reported principal directions\(^a\).

\[
\begin{array}{ccc}
g_1 & g_2 & g_3 \\
2.028(2) & 2.032(1) & 2.082(1) \\
0.645(5) & 0.0000 & 0.764(7) \\
0.0000 & 1.0000 & 0.0000 \\
0.764(7) & 0.0000 & -0.654(5) \\
\end{array}
\]

\[
\begin{array}{cccccc}
g_{\text{M1.1}} & g_{\text{M1.2}} & g_{\text{M1.3}} & g_{\text{M2.1}} & g_{\text{M2.2}} & g_{\text{M2.3}} \\
2.110 & 2.041 & 1.988 & 2.110 & 2.041 & 1.988 \\
0.5129 & 0.8499 & -0.1207 & 0.5129 & 0.8499 & -0.1207 \\
-0.5234 & 0.4198 & 0.7414 & 0.5234 & -0.4198 & -0.7414 \\
-0.6803 & 0.3185 & -0.6600 & -0.6803 & 0.3185 & -0.6600 \\
\end{array}
\]

\(^a\) The directions are given by their cosines referred to \(a^*, b\) and \(c\) axes.

ferent, symmetry related, principal directions. Since only one signal is observed, the experimental g values result from the average of the contributions of the molecular g tensors of the two magnetically non equivalent sites, \(g_{\text{M1}}\) and \(g_{\text{M2}}\).

The minimum Ni–Ni distance between non equivalent molecules is 10.64 Å, while for two equivalent sites it is 6.18 Å. Nevertheless, the fact that the EPR signals are exchange narrowed shows that intermolecular exchange interactions are operative. The g values are reasonably close to those previously observed for the analogue \((n\text{-Bu}_4\text{N})[\text{Ni/Au}(\text{dmit})_2]\)\(^{10}\). However, in that case the g values are true molecular values, because they were obtained from doped crystals. In the present case, the largest g value is observed in the \(a^*\) plane, close to the projection of the bisector of the \(\text{S}(2)–\text{Ni}–\text{S}(7)\) angle \((\approx 12^\circ)\), thus showing that also in this case the \(z\) molecular axis is in the molecular plane. Therefore it must be concluded that the unpaired electron is largely localized on the ligand, like in \((n\text{-Bu}_4\text{N})[\text{Ni/Au}(\text{dmit})_2]\). This is also in agreement with previous EPR studies of electrogenerated \([\text{M}(\text{Ph}_3\text{C}_2\text{S})(\text{dppe})]^{+}\)\(^{18}\) and \([\text{M}(\text{dmit})(\text{dppe})]^+\) species\(^{19}\). Since the unpaired electron is mainly localized on the sulfur-ligand, all these supposedly M(III) complexes should actually be regarded as M(II) species.

In order to obtain g molecular values, we assumed the principal directions of the molecular \(g_{\text{M1}}\) and \(g_{\text{M2}}\) tensors for the two non equivalent sites by analogy with \((n\text{-Bu}_4\text{N})[\text{Ni/Au}(\text{dmit})_2]\)\(^{10}\), and, from the experimental g values, we obtained the principal molecular values shown in Table IV. The agreement with \((n\text{-Bu}_4\text{N})[\text{Ni/Au}(\text{dmit})_2]\) is almost perfect, showing that the electronic structures of the two complexes are very similar one to each other. The calculated angular dependences of the \(g_{\text{M1}}\) and \(g_{\text{M2}}\) values (Fig. 5) showed that the maximum anisotropy between the two sites is \(\approx 160\) G at X-band and \(\approx 610\) G at Q-band. Since also in the 35 GHz spectra the separate resonances of the two sites are never seen, the exchange frequency is much larger than \(0.057\) cm\(^{-1}\).

The angular dependence of the linewidth shows maxima close to \(b\). Since the direction of minimum approach between the molecules is close to \(b\), it may be assumed that the broadening of the lines is essentially due to dipolar spin-spin interactions rather than to g anisotropy effects.

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