Synthesis, Molecular Structure, and Magnetic Properties of Tetraphenylarsonium Bis(*cis*-1,2-dicarbomethoxyethylenedithiolato)nickelate(III)

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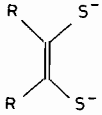
The preparation and characterization by single crystal X-ray diffraction and electron paramagnetic resonance studies of $(C_6H_5)_4As[Ni(S_2C_2(COOCH_3)_2)_2]$ *is described. Crystals of the complex belong to the triclinic space group* $P\bar{1}$, *with* $a = 10.968(3)$ Å, $b = 11.218(3)$ Å, $c = 15.561(5)$ Å, $\alpha = 86.07(4)°$, $\beta = 82.71(4)°$, $\gamma = 82.07(3)°$, *and* $\rho_{calcd} = 1.509$ g cc^{-1} *for* $Z = 2$. *The asymmetric unit contains the entire tetraphenylarsonium cation and two half anions; the nickel atoms being located on the inversion centers at (0,0,0) and (1/2,1/2,1/2). The salient structural features include an average Ni–S distance of 2.129(6) Å, an average intraligand S–Ni–S angle of 92.3(2)°, and intra- and interligand S···S separations of 3.060(9) Å and 2.965(8) Å, respectively. The two unique anions in the unit cell are nearly orthogonal and are separated by 12.14 Å. Although the two independent anions are only crystallographically required to be centrosymmetric, the immediate coordination geometry for both closely approximates* D_{2h} *symmetry, and the point symmetry for one complete anion is close to* C_{2h}. *The principal molecular g values determined from the single crystal EPR measurements are* $g_x = 2.063$, $g_y = 2.151$, $g_z = 1.986$, *where x and y bisect the intraligand and interligand S–Ni–S angles respectively. These values are in accord with the electronic structural features previously described for such square planar species.*

Introduction

The chemistry of metal complexes containing unsaturated sulfur donor ligands of general structure *1* has received considerable attention during the past fifteen years [1]. A wide variety of bis-complexes containing such metals as Fe, Co, Ni, Pd, Pt, Cu, and Au, and R = H [2, CN [3], CF_3 [4], aryl and alkyl [5], has been well documented.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Much discussion has revolved around the assignment of the metal oxidation state and the description of the ligand electronic structure in these highly delocalized square planar complexes simple molecular orbital calculations of the extended Huckel type leading to different orderings of the highest filled MOs [2a, 6]. In the case of the low spin complexes $Co(mnt)_2^{2-}$ and $Ni(mnt)_2^-$ the single crystal ESR data are best explained by a calculated MO sequence having the odd electron in an orbital of $b_{2g}(xz)$ symmetry in the D_{2h} point group and the relative magnitudes of the g and A tensor components for both these species were interpreted by Maki and coworkers [7] in terms of the ground state spin doublet $^2B_{2g}$ arising from the metal configuration $(d_{xz})^1 (d_{xy})^2$ in the hole formalism.

Very recently more detailed calculations based on the INDO approximation and including configuration interaction have been reported [8]. While these give an excited state sequence somewhat different from that given by the EHMO calculations, they predict essentially the same ground state and order of HFMO's, so that the more simple model appears adequate for the interpretation of ground state properties.

In the present paper we report the preparation and structural characterization of an analog of the $Ni(mnt)_2^-$ ion, namely an anionic nickel(III) complex *2* containing the *cis*-1,2-dicarbomethoxyethylenedithiolate ligand [9]. From EPR and magnetic measurements we find that it has electronic properties very similar to those of $Ni(mnt)_2^-$ and $Ni[S_2C_2(CF_3)_2]_2^-$ [10] and so provides further experimental confirmation of the description of the ground state electronic structure.

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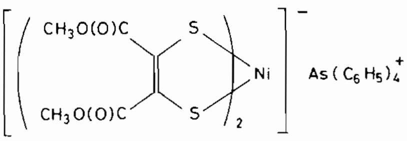

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Experimental

General Information

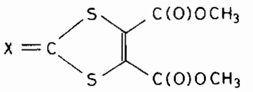
Analytical data were provided by Galbraith Laboratories, Knoxville, Tennessee and Robertson Laboratories, Florham Park, New Jersey. Dimethylacetylenedicarboxylate, ethylenetrithiocarbonate, and tetraphenylarsonium chloride hydrochloride were obtained from Eastman and used without further purification. Lithium methoxide, in methanol, was obtained from Foote Mineral Company.

Preparation of 4,5-Dicarbomethoxy-1,3-dithiol-2-thion

This compound was prepared by heating a mixture of ethylenetrithiocarbonate and dimethylacetylenedicarboxylate at 135 °C [9]. The resulting yellow product was recrystallized from acetone and melted at 87 °C. *Anal.* Calcd for $C_7H_6S_3O_4$: C, 33.59; H, 2.42; S, 38.43. Found: C, 33.75; H, 2.51; S, 38.78.

Preparation of Tetraphenylarsonium Bis(Cis-1,2-Dicarbomethoxyethylenedithiolato)Nickelate(III)

Cyclic ester *3* (X = 0) was formed in solution, by allowing 4,5-dicarbomethoxy-1,3-dithiol-2-thion, 2.00 g (0.00799 mol), in 20 ml of 1:1 THF/methanol, to react with solid mercuric acetate, 2.60 g (0.00816 mol). The two reactants were stirred rapidly for 24 hours at room temperature. A dark black precipitate formed. The precipitate was removed by filtration and a yellow-orange filtrate was obtained. The filtrate presumably contained *3* (X = 0), 0.00799 mol. Lithium methoxide, 0.61 g (0.0161 mol), in methanol, was added to the filtrate. An orange solution immediately formed. To this solution was added nickel(II) chloride hexahydrate, 0.96 g (0.00404 mol), dissolved in 10 ml of methanol whence a dark red-brown solution formed immediately. Solid tetraphenylarsonium chloride hydrochloride, 1.82 g (0.00400 mol), was then added to the nickel complex and the resulting solution was allowed to stand at room temperature for 24 hours. Large black crystals of product formed. The solution was concentrated to a volume of 10 ml at a water aspirator and more product formed. The product was filtered, dried, and recrystallized from warm acetone. The yield was 56% based upon *3* (X = S). The product melted sharply at 173.5 °C. *Anal.* Calcd for $C_{36}H_{32}O_8S_4AsNi$: C, 50.60; H, 3.78; S, 15.01; As, 8.77. Found: C, 50.75; H, 3.84; S, 14.82; As, 9.04. The ir spectrum (KBr pellet) showed a strong band at 1700 cm^{-1} (carbonyl stretch) and a strong band at 1225 cm^{-1} (C–O stretch in ester group). The visible spectrum, recorded in acetone, showed a well defined absorption band at 22,020 cm^{-1} ($\epsilon = 3{,}080$) together with a well defined shoulder at 19,400 cm^{-1}. The conductance of the complex, measured at 25 °C in nitromethane, was 41 cm^2/mol ohm, appropriate for a 1:1 electrolyte of this type.



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X-Ray Data Collection

Precession and Weissenberg photographs revealed that the black crystals of $(C_6H_5)_4As[Ni(S_2C_2(COOCH_3)_2)_2]$ belong to the triclinic system. As ultimately confirmed by the solution of the structure, the centrosymmetric group $P\bar{1}$ is correct. A crystal of dimensions 0.25 mm × 0.31 mm × 0.40 mm was oriented approximately along the crystallographic a^* axis and crystal lattice constants and the orientation matrix were determined by the accurate centering of 25 strong reflections on a CAD-4 diffractometer in the range $25° \leqslant 2\theta \leqslant 40°$. The refined cell constants and other relevant crystal data are given in Table I along with the experimental conditions for data collection.

Solution and Refinement of the Structure

The two independent nickel atoms and the arsenic atom were located from a Patterson synthesis. A structure factor calculation based on these three atoms followed by a Fourier synthesis located all of the remaining 48 nonhydrogen atoms. The structure was refined using full matrix least-squares techniques minimizing $\Sigma w(|F_o| - |F_o|)^2$ with $w^{1/2} = 2LpF_o/\sigma(I)$*. Several cycles of refinement using anisotropic thermal parameters for the nonhydrogen atoms and a fixed hydrogen atom contribution with C–H = 1.05 Å and B = 4.0 led to the final agreement factors shown in Table I. A final difference Fourier map indicated no peaks larger than 0.69 e/Å^3.

Magnetic Measurements

Susceptibility measurements were made on powder samples using a PARR Vibrating Sample Magnetometer Model 155 over a temperature range from 250 to 3 K. The complex was found to obey the Curie-Weiss law with a value of $\theta = -2°$ being derived from the complete set of data. For the low temperature data from 3 to 20 K an excellent fit with $\theta = 0°$ was obtained, indicating very little, if any, magnetic exchange between neighboring complex anions. The magnetic moment μ was found to

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*Prewitt's SFLS5 full-matrix least-squares routine.

TABLE I. Experimental Details of the X-Ray Diffraction Study of $(C_6H_5)_4As^+Ni[S_2C_2(COOCH_3)_2]_2^-$.

(A) Crystal Parameters at 20 ± 2 °C

Space Group PT

$a = 10.968(3)$ Å
$b = 11.218(3)$ Å
$c = 15.561(5)$ Å
$\alpha = 86.07(4)^\circ$
$\beta = 82.71(4)^\circ$
$\gamma = 82.07(3)^\circ$

Vol. = 1878.4 $Å^3$
$Z = 2$
Mol. Wt. = 854.4
ρ(calcd) = 1.509 g cc^{-1}
ρ(obs) = 1.48 g cc^{-1a}
$\mu = 17.0$ cm^{-1}

(B) Measurement of Intensity Data

Radiation: MoK(Zr filtered)$\lambda_{k\alpha_1} = 0.70926$ Å, $\lambda_{k\alpha_2} = 0.71354$ Å
Take-off Angle: 6.50(5) deg.
Crystal to Detector Aperture Distance: 17.3 cm
Source to Crystal Distance: 21.7 cm
Scan Type: coupled $\omega-2\theta$
Scan Range: $\Delta(2\theta) = (0.8 + 0.5 \tan\theta)$ deg. centered about the average peak position
Scan Speed: Variable from 4.0°/min to 0.61°/min, the actual value being determined from a preset intensity value and a preliminary prescan for each reflection.
Crystal Orientation: Approximately along a^*
Reflections Measured: 4578 in the region ±h, ±k, +l having $2^\circ \leqslant 2\theta \leqslant 55^\circ$.
Standard Reflections: Measured every 50 reflections; no significant deviation from average was observed.

(C) Treatment of Intensity Data

$I = [P - 2(B_1 + B_2)](FF \cdot SR)$
P = total count; B = background
SR is related to scan rate, FF is a filter factor
$\sigma(I) = [(P + 4(B_1 + B_2))(FF - SR) + (cI)^2]^{1/2}$
c = 0.045 (a factor to account for random errors other than those due to counting statistics)
Transmission Factors: Max, 0.593; Min 0.427

(D) Agreement Indicies of Least Squares Refinement

n(number of variables	455
m(number of observations)	4578
m/n(over-determination ratio)	10.1
$R = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert]$	0.066
$Rw = [\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma(F_o)^2]^{1/2}$	0.063
$S = [\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m - n)]^{1/2}$	0.94

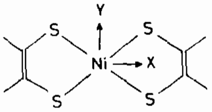
[a] Density as determined by the flotation method in a carbon tetrachloride–benzene mixture.

be 1.774 BM confirming that the complex is low spin (S = 1/2) and giving a g_{ave} value of 2.048.

EPR Measurements

Single crystal measurements were carried out at room temperature at X-band (9.5 GHz) frequency on a Varian E-12 spectrometer at the University of Nijmegen during a visit of one of us (JSW). The magnetic fields were measured with a Bruker Oscillator B-NM12 and the klystron frequencies with a Hewlett-Packard Counter HP52462. The measurements were made for three mutually orthogonal planes at intervals of 10°, the rotation axes being $\tilde{a}$, $\tilde{c}^*$ and $\tilde{a}x\tilde{c}^*$. The initial alignment of the crystals was checked by X-ray diffraction. All EPR measurements gave a single signal (there being no hyperfine structure since I = 0 for ^{58}Ni and ^{60}Ni) indicating the presence of sufficient spin–spin exchange between the two magnetically non-equivalent complex ions in the unit cell to average the two sites. Examination of a crystal at Q-band frequency indicated that the exchange was still sufficiently fast at 35 GHz to average the sites. The crystal tensor, g_c, was obtained from the rotation data via standard procedures.

Since the two magnetically non-equivalent complex ions in the unit cell are also crystallographically non-equivalent (both having a center of symmetry but one approximating C_{2h} point symmetry), in principle the crystal tensor g_c is an average of two non-equivalent molecular g tensors. However, since the coordination spheres for both complexes are very similar and possess close to D_{2h} symmetry it is reasonable to assume g-tensor equivalence. The crystal tensor can then be written as $\tilde{g}_c = \tilde{g}_{mol} + \tilde{R}\, g_{mol}\, \tilde{R}^{-1}$ where g_{mol} is the molecular tensor in the coordinate system used to define $\tilde{g}_c$ and $\tilde{R}$ is the rotation matrix which transforms one complex ion into the other. The components of $\tilde{g}_{mol}$ in the crystal coordinate system were thus derived from the above equation and the principal values obtained upon diagonalization were found to be $g_x = 2.063$, $g_y = 2.151$, $g_z = 1.986$ where the magnetic axes x, y, z were calculated to be within 3–4° of the molecular coordinate system depicted below (*4*) with z perpendicular to the $Ni–S_4$ plane**.



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Results and Discussion

The *cis* 1,2-dicarbomethoxyethylenedithiolate ligand, cmt^{2-}, was formed in solution by allowing 4,5-dicarbomethoxy-1,3-dithiol-2-one *3* (X = O) to react with lithium methoxide. Cyclic ester *3* (X = O) was formed by desulfurization of 4,5-dicarbomethoxy-1,3-dithiol-2-thion *3* (X = S) [11] with mercuric acetate [12]. It was not possible to prepare *3* (X = O) in pure form. When nickel(II) chloride hexahydrate was allowed to react with stoichiometric

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**In the present example, the $Ni–S_4$ planes of the two complex ions are almost orthogonal and have their y axes in common. Since $g_{xx} \simeq g_{zz} < g_{yy}$, the crystal tensor, g_c thus reflects the molecular tensor quite closely.

amounts of cmt^{2-} and tetraphenylarsonium chloride a solid crystalline product of composition $(C_6H_5)_4$AsNi(cmt)$_2$ was obtained.

When *3* (X = S) was used as the source of cmt^{2-} the Ni(III) complex could not be obtained in solid form. The black oils which resulted probably contained systems wherein cmt^{2-} as well as $(CH_3O)_2$C=S, formed by methoxide cleavage of *3* (X = S), were competing for the nickel.

Attempts to prepare a series of crystalline complexes containing cmt^{2-} with metals such as Fe, Co, Cu, Hg, and Au were not successful. Oils or polymeric solids were frequently encountered.

The nickel complex is formulated as *2* based upon the analytical and conductivity data, and on the basis of susceptibility and EPR data as being low-spin, with an S = 1/2 ground state.

Perspective views of the two independent Ni(cmt)$_2^-$ anions centered at 0,0,0 and 1/2,1/2,1/2 are displayed in Fig. 1. Figure 2, which is nearly a *b* axis projection, shows the packing arrangement of the $(C_6H_5)_4As^+$ ions with the two crystallographically independent Ni(cmt)$_2^-$ ions. Selected bond distances and angles are given in Table III.

Structure of the Ni(cmt)$_2^-$ Anions

The fact that the two nickel atoms lie on centers of inversion necessitates the immediate coordination geometry around these atoms to be perfectly planar. As the values for the intra- and inter-ligand S–S distances and S–Ni–S angles (Tables III and IV) indicate, the NiS_4 core is nearly an ideal square plane. This result is consistent with the geometry of other transition metal dithiolato chelates. Crystallographic investigations of the monomeric $[M(S_2C_2R_2)_2]^x$ systems with M = Co, Ni, Cu, Pd, Pt, Au and x = 0, −1, −2, all reveal the same basic square planar geometry. The fine structural features of the MS_4 core, however, exhibit trends consistent with the electronic structure of each particular four coordinate transition metal ion or molecule. The average Ni–S bond distances for the series $[Ni(S_2C_2R_2)]^x$ (x = −2, −1 and 0) are 2.17(1) Å, 2.14(1) Å, and 2.11(1) Å, respectively (Table IV). This trend is reasonable, assuming the additional electrons of the negatively charged complexes reside in a molecular orbital of M–S antibonding character.

Unlike the monoanions $[Ni(S_2C_2(CN)_2)_2]^-$ and $[Ni(S_2C_2(CF_3)_2)_2]^-$ which are stacked in the solid state with less than 4.4 Å and 3.9 Å, respectively between the planar units, the nearly orthogonal independent $[Ni(S_2C_2(COOCH_3)_2)_2]^-$ units are well separated, by *b* = 11.218(3) Å for the anions centered at 0,0,0 by *c* = 15.561 for the anions centered at 1/2,1/2,1/2, and by 12.14 Å for the two independent nickel ions. The magnitudes of these distances indicate that there should be little magnetic exchange between neighboring complex ions, a result which is confirmed by the susceptibility measurements. As noted however, the exchange is sufficient to give an averaged EPR signal.

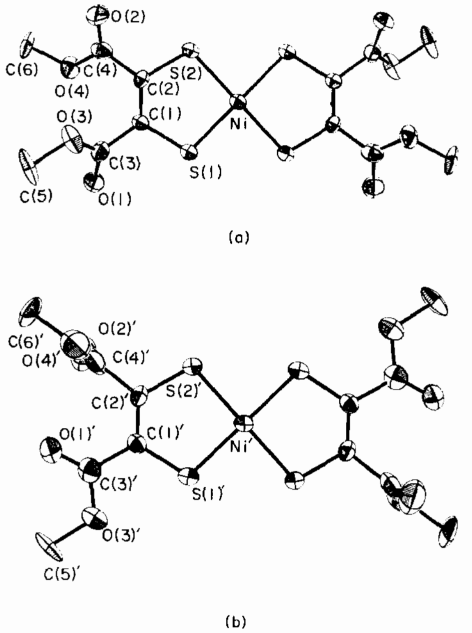

Fig. 1. Perspective views of the Ni(cmt)$_2^-$ anions: (a) centered at 0,0,0, (b) centered at 1/2,1/2,1/2. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown.

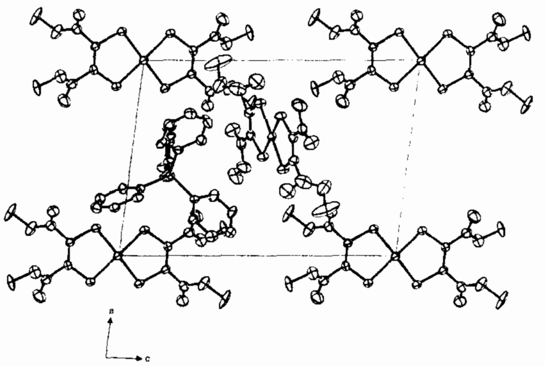

Fig. 2. A projection of the $(C_6H_5)_4As[Ni(S_2C_2(COOCH_3)_2)_2]$ unit cell contents approximately along the crystallographic *b* axis.

Although the complexes are crystallographically required to possess only $C_i(\bar{1})$ symmetry, that located at the origin comes close to possessing C_{2h} symmetry; the pseudo C_2 axis bisecting the intraligand S–Ni–S angles. For this complex the two crystallographically independent carbomethoxy (-$COOCH_3$) groups make dihedral angles of *ca.* 60° with the NiS_4 plane, while for the complex located at (1/2,1/2,1/2) the two planar independent-$COOCH_3$ groups are mutually orthogonal, with one being essentially coplanar with

TABLE II. Positional Parameters × 10^4 and Thermal Parameters ($Å^2$) × 10^3 for $(C_6H_5)_4As^+Ni[S_2C_2(COOCH_3)_2]_2^-$[a].

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
AS[b,c]	30890(5)	46462(5)	15381(4)	374(3)	428(4)	387(3)	−54(3)	−29(3)	−15(3)
R1C1	1910(5)	4421(5)	2514(3)	39(3)	64(4)	52(4)	−20(3)	−1(3)	−1(3)
R1C2	2295(5)	3639(7)	3177(4)	84(4)	190(1)	63(5)	−30(4)	−14(4)	66(5)
R1C3	1444(7)	3541(8)	3932(4)	84(6)	247(10)	50(5)	−36(6)	2(5)	56(5)
R1C4	256(7)	4154(7)	3983(4)	72(5)	153(7)	54(5)	−43(5)	−4(4)	3(5)
R1C5	−91(5)	4885(5)	3302(5)	67(4)	63(4)	92(5)	−12(3)	7(4)	−26(4)
R1C6	722(5)	5049(5)	2568(4)	57(4)	67(4)	52(4)	−19(3)	6(3)	−5(3)
R2C1	4148(5)	3171(5)	1399(3)	37(3)	46(4)	61(4)	2(3)	−0(3)	0(3)
R2C2	5391(5)	3143(5)	1330(3)	32(3)	58(4)	63(4)	5(3)	7(3)	2(3)
R2C3	6145(5)	1994(6)	1243(4)	55(4)	76(5)	97(5)	−30(4)	1(3)	22(4)
R2C4	5600(6)	980(5)	1223(4)	52(4)	52(4)	126(6)	7(3)	1(4)	18(4)
R2C5	4340(6)	1033(5)	1298(5)	66(5)	42(4)	156(7)	−18(4)	−14(5)	11(4)
R2C6	3582(5)	2123(6)	1396(4)	46(4)	55(4)	130(6)	−6(3)	−11(4)	12(4)
R3C1	4082(4)	5862(5)	1704(3)	35(3)	57(4)	57(4)	−8(3)	−1(3)	−13(3)
R3C2	4219(5)	6794(5)	1071(3)	60(4)	44(3)	60(4)	−19(3)	8(3)	5(3)
R3C3	4947(5)	7658(5)	1256(4)	64(4)	72(5)	67(4)	−10(3)	1(3)	−11(3)
R3C4	5521(5)	7572(5)	1988(4)	69(4)	55(4)	86(5)	−19(3)	−10(4)	−14(4)
R3C5	5375(6)	6641(6)	2611(4)	112(5)	81(5)	72(5)	−37(4)	−50(4)	11(4)
R3C6	4628(5)	5784(5)	2481(4)	72(4)	74(4)	59(4)	−24(4)	−11(4)	−2(3)
R4C1	2309(4)	5069(5)	521(3)	46(3)	55(3)	46(4)	−4(3)	−11(3)	−6(3)
R4C2	2476(5)	4261(5)	−123(4)	65(4)	59(4)	47(4)	−10(3)	−7(3)	−16(3)
R4C3	1172(6)	5718(6)	−971(4)	68(5)	71(5)	73(4)	−20(4)	−24(4)	24(4)
R4C4	1892(6)	4584(6)	−885(4)	75(5)	77(5)	59(4)	−13(4)	−15(4)	−2(4)
R4C5	968(5)	6553(5)	−300(4)	49(4)	51(4)	55(5)	−8(3)	−2(4)	2(4)
R4C6	1575(5)	6204(5)	471(3)	49(4)	52(4)	73(4)	−2(3)	1(3)	0(3)
NI[c]	0	0	0	406(6)	472(6)	438(6)	−84(5)	8(5)	−27(5)
S1	−1219(1)	−926(1)	905(1)	41(1)	60(1)	52(1)	−14(1)	−2(1)	6(1)
S2	1406(1)	−235(1)	848(1)	45(1)	69(1)	49(1)	−21(1)	−4(1)	3(1)
C1	−397(4)	−1278(4)	1780(3)	41(3)	50(3)	48(4)	−11(3)	0(3)	−1(3)
C2	726(5)	−990(4)	1746(3)	51(3)	49(3)	38(3)	−6(3)	−11(3)	−6(3)
C3	−1124(5)	−1847(6)	2529(4)	58(4)	67(4)	55(4)	−2(3)	−13(3)	4(4)
C4	1520(5)	−1275(5)	2456(4)	62(4)	70(4)	63(4)	−22(3)	4(3)	−19(3)
C5	−1829(7)	−1661(6)	4049(4)	169(7)	102(6)	54(4)	−3(5)	54(4)	26(4)
C6	2017(6)	−2600(5)	3689(4)	132(5)	96(5)	48(4)	−5(4)	−54(4)	18(3)
O1	−1658(4)	−2699(4)	2517(3)	95(3)	98(3)	83(3)	−58(3)	−21(3)	22(3)
O2	2222(4)	−609(4)	2644(3)	120(4)	115(4)	99(4)	−71(3)	−46(3)	27(3)
O3	−1112(4)	−1238(3)	3230(3)	116(4)	61(3)	67(3)	−12(2)	24(3)	5(2)
O4	1384(3)	−2313(3)	2894(2)	100(3)	46(3)	74(3)	−19(2)	−23(2)	9(2)
NIP[c]	5000	5000	5000	407(4)	474(6)	447(6)	−103(5)	−49(5)	13(5)
S1P	4355(1)	3368(1)	4759(1)	48(1)	58(1)	74(1)	−19(1)	−1(1)	−8(1)
S2P	6821(1)	4376(1)	4421(1)	44(1)	56(1)	82(1)	−13(1)	5(1)	−14(1)
C1P	5617(5)	2553(5)	4219(3)	59(4)	50(4)	50(3)	−13(3)	−8(3)	−7(3)
C2P	6685(5)	3000(5)	4083(3)	51(4)	59(4)	60(4)	2(3)	3(3)	−18(3)
C3P	5479(7)	1358(6)	3915(4)	85(5)	84(5)	53(4)	−14(4)	−14(4)	−10(4)
C4P	7933(8)	2333(7)	3644(7)	107(7)	61(6)	165(9)	−21(5)	−36(7)	−39(7)
C5P	4154(7)	−126(6)	3852(5)	165(7)	75(5)	127(6)	−65(5)	−51(5)	−33(4)
C6P	9505(8)	1621(7)	2692(7)	121(7)	105(7)	375(15)	4(6)	137(9)	−100(8)
O1P	6306(4)	717(4)	3529(3)	108(4)	75(3)	120(4)	−23(3)	13(3)	−35(3)
O2P	8561(5)	1648(5)	4177(4)	118(5)	143(5)	151(6)	20(4)	−22(4)	−56(4)
O3P	4349(4)	1054(4)	4125(3)	86(3)	89(3)	119(4)	−35(3)	−19(3)	−27(3)
O4P	8172(6)	2501(5)	2875(4)	165(5)	139(5)	93(4)	−71(4)	30(4)	−29(4)

[a] Thermal parameters correspond to the expression $T = -[8\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^* + \ldots)]$. Estimated standard deviations in parentheses. [b] Positional parameters for this atom are ×10^5. [c] Thermal parameters for this atom are ×10^4.

the NiS_4 unit. This complex ion has only C_i symmetry therefore. This difference in orientation of the carbomethoxy groups is reflected in the C–O distances, the C(4)′–O(2)′ and C(4)′–O(4)′ distances being nearly equal and the O(4)′–CH_3 bond being exceptionally long. The C–O bond distances for

TABLE III. Selected Bond Distances (Å) and Angles (deg.) for $(C_6H_5)_4As[Ni(S_2C_2(COOCH_3)_2)_2]$[a].

Distances C_{2h}[b]		C_i[c]	
Ni–S(1)	2.136(1)	Ni′–S(1)′	2.121(1)
Ni–S(2)	2.130(1)	Ni′–S(2)′	2.129(1)
S(1)–C(1)	1.717(5)	S(1)′–C(1)′	1.710(5)
S(2)–C(2)	1.717(5)	S(2)′–C(2)′	1.699(6)
C(1)–C(2)	1.326(7)	C(1)′–C(2)′	1.328(8)
C(1)–C(3)	1.491(8)	C(1)′–C(3)′	1.503(8)
C(2)–C(4)	1.479(7)	C(2)′–C(4)′	1.526(11)
C(3)–O(1)	1.183(7)	C(3)′–O(1)′	1.187(8)
C(4)–O(2)	1.192(7)	C(4)′–O(2)′	1.263(11)
C(3)–O(3)	1.321(7)	C(3)′–O(3)′	1.324(8)
C(4)–O(4)	1.329(7)	C(4)′–O(4)′	1.222(13)
O(3)–C(5)	1.487(8)	O(3)′–C(5)′	1.462(8)
O(4)–C(6)	1.467(7)	O(4)′–C(6)′	1.642(10)
As–R1C(1)		1.884(5)	
As–R2C(1)		1.899(5)	
As–R3C(1)		1.905(5)	
As–R4C(1)		1.892(5)	

Angles C_{2h}[b]		C_i[c]	
S(1)–Ni–S(2)	92.15(6)	S(1)′–Ni′–S(2)′	91.51(6)
Ni–S(1)–C(1)	104.9(2)	Ni′–S(1)′–C(1)′	104.1(2)
Ni–S(2)–C(2)	105.2(2)	Ni′–S(2)′–C(2)′	103.9(2)
S(1)–C(1)–C(2)	120.2(4)	S(1)′–C(1)′–C(2)′	119.8(4)
S(2)–C(2)–C(1)	120.9(4)	S(2)′–C(2)′–C(1)′	120.7(4)
S(1)–C(1)–C(3)	112.9(4)	S(1)′–C(1)′–C(3)′	119.0(4)
S(2)–C(2)–C(4)	114.7(4)	S(2)′–C(2)′–C(4)′	114.2(5)
C(1)–C(2)–C(4)	124.3(5)	C(1)′–C(2)′–C(4)′	125.0(6)
C(2)–C(1)–C(3)	126.8(5)	C(2)′–C(1)′–C(3)′	121.2(5)
C(1)–C(3)–O(1)	126.1(5)	C(1)′–C(3)′–O(1)′	123.7(6)
C(2)–C(4)–O(2)	124.2(5)	C(2)′–C(4)′–O(2)′	116.8(8)
C(1)–C(3)–O(3)	109.5(5)	C(1)′–C(3)′–O(3)′	112.3(5)
C(2)–C(4)–O(4)	113.9(5)	C(2)′–C(4)′–O(4)′	117.0(8)
O(1)–C(3)–O(3)	124.4(6)	O(1)′–C(3)′–O(3)′	124.1(6)
O(2)–C(4)–O(4)	121.9(5)	O(2)′–C(4)′–O(4)′	126.2(9)
C(3)–O(3)–C(5)	116.4(5)	C(3)′–O(3)′–C(5)′	116.4(5)
C(4)–O(4)–C(6)	117.9(4)	C(4)′–O(4)′–C(6)′	101.2(7)
R1C(1)–As–R2C(1)		107.3(1)	
R1C(1)–As–R3C(1)		111.6(1)	
R1C(1)–As–R4C(1)		110.6(1)	
R2C(1)–As–R3C(1)		104.5(1)	
R2C(1)–As–R4C(1)		110.0(1)	
R3C(1)–As–R4C(1)		108.9(1)	

[a] Standard deviations in parentheses. All C–C distances and angles of the tetraphenylarsonium cation are included in the supplementary material. [b] Results for anion centred at (0,0,0) with approximate C_{2h} symmetry. [c] Results for anion centered at (1/2,1/2,1/2) with C_i symmetry only.

the group coplanar with the nickel–sulfur plane on the other hand agree more closely with the normal values for such bonds as do the distances for these groups in the complex located at the origin. Apart from suggesting that there are different conjugative effects involved between the-$COOCH_3$ groups and the dithiolate system—or lack thereof for the orthogonally oriented group—we have no alternative explanation of the differences in bond distances.

As indicated in the experimental section, the susceptibility and EPR data demonstrate that the ground state for the $\mathrm{Ni(cmt)}_2^-$ ion is an $S = 1/2$ Kramers doublet, while for the principal axes of the g tensor, we find $g_y > g_x > g_z$, for the coordinate system illustrated previously, the magnitudes being very close to those observed by Maki *et al.* for $\mathrm{Ni(mnt)}_2^-$ [7].

As noted in the Introduction these results are consistent with a $^2B_{2g}$ ground state, the electron configuration in the hole formalism being $(xy)^2$-$(xz)^1$, and together with the form of the visible spectrum we conclude that the electronic properties of $\mathrm{Ni(cmt)}_2^-$ closely parallel those of the anionic d^7 square planar dithiolate systems that have been characterized to date.

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TABLE IV. Important Intramolecular Distances (Å) for Bis 1,2-Dithiolene Complexes of Ni.

Complex	Ni–S	S–S (intra)	S–S (inter)	S–C	C–C (chelate ring)	Ref.
$[Ni(S_2C_2(CN)_2)_2]^{2-}$	2.165(9)	3.101(7)	3.022(7)	1.75(2)	1.33(2)	13, 14
$[Ni(S_2C_2(COOCH_3)_2)_2]^-$	2.129(6)	3.060(9)	2.965(8)	1.711(8)	1.327(8)	this work
$[Ni(S_2C_2(CN)_2)_2]^-$	2.147(4)	3.095(3)	2.967(3)	1.714(4)	1.356(7)	15
$[Ni(S_2C_2(CF_3)_2)_2]^-$	2.135(4)	3.057(3)	2.981(3)	1.70(2)	1.40(2)	9
$Ni(S_2C_2(C_6H_5)_2)_2$	2.101(2)	2.966(4)	2.967(4)	1.71(1)	1.37(1)	16, 17
$Ni(S_2C_2(CF_3)_2)_2$	2.122(3)	3.013(5)	2.989(5)	1.71(1)	1.38(2)	18

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