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Contribution from the Department of Chemistry,
University of Iowa, Iowa City, Iowa 52242

Metal Dithiosquarates. II.[1] Synthesis and Characterization of Bis(Dithiosquarato) Tetrahedral and Planar Complexes. Crystal and Molecular Structure of Potassium Bis(dithiosquarato)nickelate(II) Dihydrate

D. COUCOUVANIS,*[2] D. G. HOLAH,[3] and F. J. HOLLANDER

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The synthesis and characterization of the dithiosquarate dianion, $(S_2C_4O_2)^{2-}$, and the four-coordinate sulfur-bonded complexes of this chelating ligand are reported. An unusually large intraligand S–S distance, "bite", dominates the chemistry of the new ligand. Electronic, magnetic, and solid-state properties suggest tetrahedral structures for the $[M(S_2C_4O_2)_2]^{2-}$ complexes with M = Zn(II), Co(II), Fe(II), and Mn(II). Planar structures are adapted by the analogous Ni(II), Pd(II), Pt(II), and Cu(II) complexes. The potassium bis(dithiosquarato)nickelate(II) dihydrate $(K_2M(S_2C_4O_2)_2 \cdot 2H_2O)$ crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell. The cell dimensions are $a = 7.871$ (5) Å, $b = 15.222$ (11) Å, $c = 6.406$ (3) Å, and $\beta = 95.58$ (3)°. Intensity data were collected with a four-circle computer-controlled diffractometer using the θ–2θ scan technique. Refinement by full-matrix least squares of 105 parameters on 583 data gave a final R value of 0.018. The nickel atom is rigorously planar and four-coordinated by the S–S "bites" of two dithiosquarate ligands. Values of selected structural parameters are as follows: Ni–S, 2.212 (1), 2.234 (2) Å; C–S, 1.688 (4), 1.695 (4) Å; S–S(bite), 3.257 (2) Å; S–Ni–S(intraligand), 94.19 (6)°; S–S(interligand), 3.027 (2) Å; S–Ni–S(interligand) 85.81 (5)°.

Introduction

The stereochemistry of monomeric bis(chelate)metal(II) dithiolene[4] and 1,1-dithio[5] complexes is characterized by a dominance of planar structures.[6]. By contrast, the tetrahedral geometry is more frequently observed in four-coordinate metal complexes with oxygen and nitrogen chelates. In the latter the type of coordination adopted by a metal ion depends on both the steric characteristics of the ligands and the type of metal ion.[7]

A geometric constraint inherent in the structures of the 1,1-dithio chelates is the S–S intraligand distance (2.80 Å). A short "bite" may be one of the principal reasons for the pronounced tendency of the 1,1-dithio chelates to (a) stabilize metal ions in high formal oxidation states and (b) form planar complexes with bivalent, first-row transition metal ions and octahedral or distorted octahedral complexes with trivalent ions.

Some deviations from the general stereochemical trends characteristic of sulfur chelates are found with chelating ligands in which the S–S bite is greater than 3 Å.

Spectroscopic and magnetic properties of monomeric bis(chelate)metal(II) complexes with the difluorodithiophosphate $(S_2PF_2^-)$ anion suggest tetrahedral geometry for the MS_4 chromophore[8] (M = Co(II), Fe(II), Mn(II)). Similarly with the structurally related diethyldithiophosphinate ligand $(S_2PEt_2^-)$, tetrahedral Co–S_4 and Zn–S_4 units have been found in dimeric complexes.[9]

Recently, Davison and Switkes[10] reported on the synthesis and characterization of bis(imidodithiophosphinato)complexes, $((R_2PS)_2N)_2M$; M = Fe, Ni, Co; R = C_6H_5, CH_3. The tetrahedral structures proposed for the NiS_4 and FeS_4 structural units have been verified[11,12] by X-ray crystallography.

The synthesis and structural characterization of the analogous tetrahedral Mn(II) complex also has been reported.[13] A common feature in the structures of these complexes is the unusually large S–S bite of the imidodithiophosphinate ligand, which varies from 4.16 Å in the iron(II) complex to 3.49 Å in the nickel(II) complex.

The unusually large bite of the imidodithiophosphinate ligand in high-spin tetrahedral complexes led us to an exploration of the bite size effect in the stabilization of low oxidation states and tetrahedral geometry in high-spin sulfur chelate complexes.

The hitherto unknown ligand dithiosquarate was synthesized[1,18] for the following reasons: (A) the cyclobutene ring steric constraints require a large intramolecular S–S distance; (B) the rigidity of the molecule will not allow for a facile intraligand S–S oxidation. Interest in the synthesis of low-valent metal–sulfur complexes with tetrahedral stereochemistry derives from the novelty of these species and the apparent importance of metal–sulfur tetrahedral coordination in certain nonheme iron proteins.

Structural studies on the oxidized form of rubredoxin, an iron–sulfur protein, have shown the iron atom tetrahedrally coordinated by four cysteinyl sulfurs.[14] Attempts to prepare synthetic analogs of the iron core,[15] with simple sulfur ligands (i.e., L-cysteine) thus far have been unsuccessful.

An attempt to simulate the iron core in rubredoxin was described by Anglin and Davison.[16] The ligand employed in their study was the dodecapeptide (Gly-Cyl-Gly)$_4$ protected at the N and C termini by *tert*-butyloxycarbonyl and amide functions, respectively.

The coordination properties of this potentially tetradentate sulfur chelate were studied in dimethyl sulfoxide solution, with Fe(II) and Co(II) ions. The electronic spectra of these solutions were indicative of tetrahedrally coordinated high-spin Fe(II) and Co(II) complexes.

Recently syntheses and structures of complexes containing tetrahedrally coordinated iron(III) with a dimeric Fe_2S_2 core have been reported. Their relevance as synthetic analogs for the active sites of certain iron–sulfur proteins was discussed. In one of these complexes, bis(μ-sulfido-*o*-xylyl-α,α'-dithiolato)ferrate(III), the dithiolate ligand was characterized by an S–S bite of 3.690 Å. The importance of "structured flexibility" of the chelating ligand in stabilizing the tetrahedral geometry was underscored by the authors.[17] In this paper we report on the synthesis of the dithiosquarate dianion[19] and its coordination chemistry with first-row bivalent transition metal ions. The crystal structure of the bis(dithiosquarato)nickel(II) complex was determined and is also reported.

Experimental Section

The chemicals in this research were used as purchased. Perchlorocyclobutenone was obtained from Aldrich Chemical Co., Inc. Analyses were performed by the analytical services laboratory of the Chemistry Department of the University of Iowa and melting points recorded are uncorrected.

Synthesis and Reactions of Ligand and Complexes. (I) Potassium 1,2-Cyclobutenedione-3,4-dithiolate (Potassium Dithiosquarate; K_2Dts). Diethyl squarate was prepared by refluxing 50 g (0.24 mol) of perchlorocyclobutenone for 2 hr in 250 ml of absolute ethanol. Excess ethanol and the hydrogen chloride by-product were distilled off, leaving a milky white residue. This residue was redissolved slowly in 200 ml of absolute ethanol and transferred to a 250-ml pressure-equalizing funnel for further use. Potassium metal (19 g, 0.5 g-atom) was dissolved in 550 ml of absolute ethanol in a three-neck round-bottom flask. Hydrogen sulfide was bubbled through the solution with stirring for ca. 1 hr during which time a suspension of KHS slowly formed. Excess H_2S was removed by bubbling nitrogen through the solution for about 15 min.

The ethanolic solution of diethyl squarate (see above) was added to the KHS suspension with stirring and under nitrogen over a period of ca. 3 hr. The thick yellow precipitate that formed was filtered off and was recrystallized from warm water, crystallization being effected by the addition of absolute ethanol. The product was filtered off, washed with ether, and dried under vacuum.

(II) Tetraphenylphosphonium Dithiosquarate, $(Ph_4P)_2Dts$. This salt was prepared by mixing in 2:1 ratio Ph_4PCl and K_2Dts in water. The yellow solid that precipitated immediately was isolated and recrystallized from hot acetonitrile.

(III) Potassium Bis(dithiosquarato)metalate(II) Complexes, $K_2M(Dts)_2 \cdot nH_2O$ (M = Mn, Fe, n = 4; M = Co, Ni, Zn, Pd, Pt, n = 2). A typical procedure for the synthesis of these compounds using stoichiometric quantities of reagents was as follows for the $K_2Co(Dts)_2 \cdot 2H_2O$ complex.

A solution of 0.2 g of $CoCl_2 \cdot 6H_2O$ in 2 ml of water was added to a solution of 0.45 g of K_2Dts in 3 ml of water. Reaction was immediate and crystals of the desired product separated on cooling the solution to 0°C. The product was filtered off, washed with ethanol and ether, and dried under vacuum at room temperature. In the case of iron, the same product, $K_2FeDts_2 \cdot 4H_2O$, was obtained regardless of whether the hydrates of iron(II) or iron(III) chloride were used. However, the reaction was carried out under a nitrogen atmosphere to prevent oxidation of the iron(II) complex.

This general procedure was followed with copper(II) and with copper(I) ($Cu(CH_3CN)_4ClO_4$).[20] In all cases the deep, blood red solution, which resulted upon mixing aqueous solutions of Cu(II) or Cu(I) ions and K_2Dts, deposited an insoluble brick red solid. Reproducible chemical analyses for this presumably Cu(I) compound could not be obtained.

(IV) Tetraphenylphosphonium Bis(dithiosquarato)metalate(II) Complexes, $(Ph_4P)_2M(Dts)_2$ (M = Co, Ni, Zn, Pd, Pt). These complexes were obtained in high yield by adding Ph_4PCl to aqueous solutions of the $K_2M(Dts)_2$ complexes prepared as previously described. The water-insoluble products were isolated, extracted into dimethylformamide, DMF, and crystallization was effected by the addition of a small amount of water.

(V) Tetraphenylphosphonium Bis(dithiosquarato)metalate(II), $(Ph_4P)_2Cu(Dts)_2$. Since reactions between aqueous solutions of Cu(II) and K_2Dts resulted in the formation of Cu(I) complexes (see above), the following methods were used to prepare the Cu(II) complex.

(a) To a suspension of 0.1 g of copper(II) chloride hydrate in 5 ml of hot acetonitrile was added a stoichiometric amount of $(Ph_4P)_2Dts$ in hot acetonitrile. The intensely violet solution thus obtained deposited large dark crystals following filtration, concentration, and cooling to 0°C. Recrystallization was effected from DMF in a manner previously described.

(b) Alternatively, treatment of $(Ph_4P)_2Zn(Dts)_2$ with anhydrous copper(II) chloride in acetone also produced a violet solution which deposited crystals of $(Ph_4P)_2Cu(Dts)_2$.

(VI) Tetraphenylphosphonium Bis(dithiosquarato)ferrate(II) and -manganate(II) Complexes, $(Ph_4P)_2M(Dts)_2$ (M = Fe(II), Mn(II)). The crude $(Ph_4P)_2M(Dts)_2$ complexes were obtained by mixing in stoichiometric ratios aqueous solutions of metal(II) chlorides (or $FeCl_3$) and K_2Dts, followed by addition of Ph_4PCl. The insoluble complexes which appear to be the hydrates were filtered off and dried under vacuum. All subsequent reactions were carried out in an inert atmosphere. Crystals of the dihydates were obtained after recrystallizations were carried out from wet solvents such as DMF and CH_3CN.

The crude complexes were sparingly soluble in hot ethanol from which crystals of ethanol adducts were obtained (Table VII).

Pure crystals of $(Ph_4P)_2M(Dts)_2$ (M = Fe, Mn) were obtained (a) by recrystallization of the crude material, which had been "dried" under vacuum for several hours, from either dry CH_3CN or dry CH_2Cl_2 followed by addition of ether,[21] (b) by heating under vacuum the $(Ph_4P)_2M(Dts)_2 \cdot 2EtOH$ complexes for 8 hr at 60–80°C, or (c) by the recrystallization of these materials from hot CH_3CN. The iron(II) complex was also made by the reaction of Ph_4PFeCl_4 in an ethanol–CH_2Cl_2 mixture with an ethanolic solution of $(Ph_4P)_2Dts$.

(VII) Reactions of $(Ph_4P)_2M(Dts)_2$ in Air (M = Mn, Fe). Formation of the $C_8O_4S_3{}^{2-}$ Monosulfide. Acetonitrile solutions of $(Ph_4P)_2Fe(Dts)_2$, when exposed to air, developed an intense dark green color immediately. This color slowly discharged to a pale brown with the precipitation of a dark brown material. In the case of manganese the initially bright yellow solution slowly darkened to a deep blood red color. These CH_3CN solutions of the $(Ph_4P)_2M(Dts)_2$ complexes were exposed to air for 12 hr when the solvent had essentially evaporated. The solid residues were extracted into CH_3CN and yellow crystals were formed upon addition of ether to these solutions. Even following two recrystallizations, crystals from the iron reaction had a brown tinge while those from the manganese reaction had a slight red tinge. However, X-ray powder patterns, infrared spectra, analyses, and melting points were identical for those two compounds[22] (Table V) which did not contain metal ions.

Physical Measurements. Magnetic susceptibilities were determined at ambient room temperature using a Faraday technique. The calibrant was $Hg(Co(SCN)_4)$.[23] Near-infrared spectra were obtained with a Beckman IR-20A recording spectrophotometer. Ultraviolet, visible and near-infrared spectra were obtained with a Cary Model 14 recording spectrophotometer using 1-cm quartz cells. A Debye-Scherrer camera utilizing nickel-filtered copper radiation was used to observe the X-ray powder patterns of the complexes. Nonius, Weissenberg, and precession cameras were used for the single-crystal preliminary alignments and space group determinations. Intensity data were collected on a Picker FACS I automated four-circle diffractometer equipped with a graphite single-crystal monochromator pulse height analyzer and automated by a DEC-PDP8-I and disk with FACS-I DOS software.

Conductivity studies in distilled acetonitrile or spectral grade nitromethane were performed using a Beckman Model RC 16B2 conductivity bridge and a Yellow Springs Instrument Co., Inc., 3502 conductivity cell.

Cyclic voltammetry data were obtained on a Chemtrix Model SSP-2 polarograph equipped with a Tektronix storage oscilloscope. The working electrode was a 1.0-mm diameter platinum sphere. The half-wave potentials reported have an estimated precision of 0.01 V. The potentials at which $Ni(MNT)_2{}^{2-}$ undergoes oxidation[24] were determined to be to 0.18 and +1.25 V. The electrochemistry of the complexes was studied in acetonitrile, distilled over P_2O_5, with tetra-*n*-propylammonium hexafluorophosphate as supporting electrolyte.[25]

The preparation of the Ag–AgI methylene chloride reference electrode has been described in the literature.[26] A modified version of the cell employed by Rohrscheid, et al.,[26] was used for the electrochemical measurements.

X-Ray Diffraction Measurements. Collection and Reduction of Data. Specific details concerning crystal characteristics and X-ray diffraction methodology are shown in Table I. Crystals suitable for crystallographic work were obtained by slow cooling of concentrated aqueous solutions of potassium bis(1,2-dithiosquarato)nickelate. Following preliminary alignment on a precession camera, the crystal was transferred to the diffractometer. The preliminary cell dimensions were refined on the setting angles of 12 reflections, well separated in reciprocal space, between 25 and 32° 2θ (λ(Mo Kα) 0.7107 Å), which were carefully centered in the receiving aperture of the detector.

Intensity data[27] were obtained by the moving crystal–moving counter technique. A scan speed of 1°/min was used and the background for each reflection was determined by 10-sec counts at

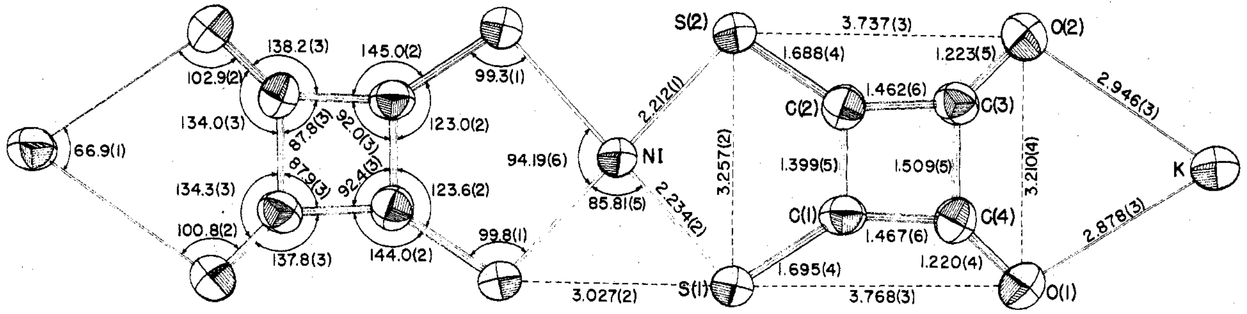

Figure 1. The molecular structure of $K_2Ni(S_2C_4O_2)_2\cdot 2H_2O$. The nickel atoms sit on a crystallographic center of symmetry. The esd's of the least significant digit(s) of the distances (Å) and angles (deg) are given in parentheses. The thermal ellipsoids as drawn by ORTEP[33] represent the 50% probability surfaces, and the complete coordination sphere of the potassium as well as the interactions of the water molecules has been left out for clarity. See also Table III for other distances and angles.

Table I. Crystal Intensity Measurement and Structure Determination Data

Empirical formula	$K_2NiS_4O_6C_8H_4$	Reflections measd[d]	1424
Mol wt	460.7	Takeoff angle	3.0°
Cell dimensions	$a = 7.871 \pm 0.005$ Å	2θ range	$0° < 2\theta < 40°$
	$b = 15.222 \pm 0.011$ Å	Scan width[e]	1.1°
	$c = 6.406 \pm 0.003$ Å	Unique reflections	707
	$\beta = 95.58 \pm 0.03°$	Atoms in asymmetric unit	12
Obsd density	2.03 ± 0.05 g cm^{-3} [a]	Final R_1	0.018
		Final R_2	0.020
Calcd density	2.00 g cm^{-3}	Reflections used in refinement	583
Z	2	No. of parameters	105
Space group	$P2_1/c$[b]	SDOUW[f]	0.73
λ(Mo Kα)	0.7107 Å[c]		
μ, cm^{-1}	23.3		
Crystal dimensions, mm	0.1 × 0.1 × 0.25		

[a] Determined by pycnometry. [b] Systematic absences: $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$. [c] A graphite single-crystal monochromator was used. [d] Reflections which exceeded a counting rate of 10,000 Hz at the peak were remeasured with a zirconium attenuator in the diffracted beam. [e] A θ-2θ scan technique was used. The base width was expanded at the high-2θ side to allow for a_1-a_2 dispersion. [f] Standard deviation of a reflection of unit weight.

either end of the scan range. Three "standard" reflections were measured after every 100 data points to monitor instrumental and crystal stability. Their intensities showed no systematic variation over the data collection period, and random variations were within the range predicted by counting statistics. Net intensities and their standard deviations were calculated according to the formulas

$$I = C - \frac{t_c}{2t_b}(B_1 + B_2)$$

$$\sigma^2(I) = C + \frac{t_c^{\,2}}{4t_b^{\,2}}(B_1 + B_2)$$

where C is the total count over the peak, taken for scan time t_c, and B_1 and B_2 are background counts, each taken for time t_b. Lorentz and polarization factors were then applied to the data (including the polarization factor for the monochromator). Equivalent data were averaged and assigned standard deviations as the larger of $\sigma(I_{av}) = (\sum\sigma^2(I))^{1/2}/N$ or $\sigma(I_{av}) = (\sum(I - I_{av})^2)^{1/2}/(N-1)$ where N is the number of reflections being averaged. The least-squares program used minimized the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$. The weighting scheme used gave $w = 0.0$ to those reflections with $F^2 < 3\sigma'(F^2)$ and $w = 1/\sigma^2(F)$ to all other reflections. Finite differences were used to calculate $\sigma(F)$ from $\sigma(F^2)$ and F^2: $\sigma(F) = F - [F^2 - \sigma'(F^2)]^{1/2}$, $\sigma'^2(F^2) = \sigma^2(F^2) + (pF^2)^2$, where the "ignorance factor" p was 0.04 at first but was reduced to 0.02 in the last stages of refinement, $\sigma(F^2) = (Lp)^{-1}\sigma(I)$.

The scattering factors for the neutral atoms were taken from the tabulation of Doyle and Turner.[28] Real and imaginary dispersion terms[29] for all atoms were included in the calculations. The best-fit spherical scattering factor of Stewart et al.[30] was used for the hydrogen atoms. A calculation of the absorption corrction for a few reflections showed that they varied by only 10% in the intensity, due to the small size and regularity of the crystal, and no absorption corrections were applied to the data.

Structure Determination and Refinement. In space group $P2_1/c$, two molecules of the compound in the cell implied that the nickel atom had to be on the center of symmetry at the origin. A three-dimensional Patterson synthesis was interpreted to give the correct positions of the two sulfur atoms, in addition to the nickel at the origin, and an incorrect position for the potassium atom. A Fourier map phased on the refined values of these input parameters revealed the correct location of the potassium and the rest of the dithiosquarate ligand. A subsequent difference Fourier map revealed the water molecule.

Refinement of all heavy atoms with anisotropic thermal parameters converged to an R value of 0.022, and a difference Fourier showed two clear peaks near the oxygen of the water molecule, which were put into the least-squares procedure as hydrogen atoms and refined with isotropic thermal parameters. Refinement of all atoms converged rapidly and in the last cycle of least squares no parameter shifted by more than 5% of its esd as calculated from the inverse least-squares matrix. The largest peak on the final difference Fourier was 0.2 e/Å^3 in height and was uncorrelated with the structure. Inspection of the values of F_o and F_c after the last cycle showed no indications of secondary extinction. The final values of R_1 and R_2 and the standard deviation of unit weight[31] for 105 parameters refined on 583 "observed" data were 0.018, 0.020, and 0.073.

The final values of the atomic parameters are given in Table II together with their esd's. A table of the observed structure factors, their esd's and the differences $|F_o| - |F_c|$ is available.[32]

Results and Discussion

(A) Structure of the $Ni(Dts)_2^{2-}$ Complex. Atomic positional parameters with standard deviations derived from the inverse matrix of the last least-squares refinement are compiled in Table II. Intramolecular bond distances and angles are given[33] in Figure 1 and Table III.

The nickel atom, on a crystallographic center of symmetry, is coordinated in a planar fashion by the sulfur atoms of two ligands and shows no axial interactions. The exterior angles at the two carbon atoms attached to sulfur are highly distorted from the "ideal" value of 135° to reduce the sulfur–sulfur bite distance to its observed value of 3.26 Å. The quite large oxygen–oxygen bite distance of 3.21 Å, however, is essentially unperturbed. The carbon–carbon, carbon–sulfur, and carbon–oxygen bond lengths are compatible with a description of the anion that gives greatest weight to resonance form a with significant contributions from b and c (see Figure 2).

The NiS_4 and $S_2C_4O_2$ molecular fragments are individually planar but not coplanar and define a dihedral angle of 1.22° in the slightly "stepped"[7] structure.

The structural features of the ligand are compared to those found in the structure of the $Cu_8(Dts)_6^{4-}$ complex[34] (Table IV). The constancy of the cyclobutenone intra-ring angles is

Table II. Positional and Thermal Parameters and Their Standard Deviations in Potassium Bis(dithiosquarato)nickelate(II) Dihydrate[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	2.56 (3)	2.04 (3)	2.50 (4)	−0.01 (2)	−0.21 (2)	0.05 (2)
K	0.5552 (1)	0.14783 (5)	−0.0104 (1)	4.60 (5)	2.45 (3)	3.24 (5)	0.14 (3)	−0.38 (4)	0.07 (3)
S(1)	0.1178 (1)	0.12868 (5)	0.1000 (2)	3.79 (5)	2.32 (4)	3.16 (5)	−0.33 (3)	−0.86 (4)	0.37 (3)
S(2)	0.1119 (1)	−0.07098 (5)	0.2818 (2)	3.81 (4)	2.04 (4)	3.04 (5)	−0.15 (3)	−0.52 (4)	0.15 (3)
O(1)	0.4141 (4)	0.1936 (2)	0.5724 (4)	5.0 (1)	2.9 (1)	4.1 (1)	−1.1 (1)	−1.2 (1)	0.1 (1)
O(2)	0.3955 (3)	−0.0022 (2)	0.7554 (4)	4.1 (1)	3.0 (1)	3.2 (2)	0.1 (1)	−0.7 (1)	0.2 (1)
C(1)	0.2228 (4)	0.0979 (2)	0.3321 (6)	2.5 (1)	2.1 (1)	3.2 (2)	0.1 (1)	0.2 (1)	0.3 (1)
C(2)	0.2176 (4)	0.0123 (2)	0.4108 (6)	2.4 (1)	2.5 (2)	2.7 (2)	0.2 (1)	0.1 (1)	−0.1 (1)
C(3)	0.3301 (4)	0.0349 (2)	0.5983 (7)	2.6 (2)	2.4 (2)	2.7 (2)	0.4 (1)	0.1 (2)	0.2 (2)
C(4)	0.3377 (4)	0.1270 (2)	0.5129 (6)	2.4 (2)	2.7 (2)	2.8 (2)	−0.4 (1)	−0.1 (2)	−0.1 (1)
O(3)	0.7663 (4)	0.2173 (2)	0.3359 (6)	5.6 (2)	3.7 (1)	4.0 (2)	0.4 (1)	−0.2 (1)	0.8 (1)
H(1)	0.89 (1)	0.212 (5)	0.29 (1)	13.7 (24)					
H(2)	0.787 (7)	0.194 (3)	0.430 (8)	4.9 (15)					

[a] Calculated standard deviations are indicated in parentheses. The thermal parameters (B) are in units of Å^2. The temperature factor has the form $T = \exp[-\Sigma(^1/_4 B_{ij}H_iH_ja_i{}^*a_j{}^*)]$ for the anisotropic case and $T = \exp[-B((\sin\theta)/\lambda)^2]$ for the isotropic case. H is the Miller index, a^* is the reciprocal cell length, i and j are cycled 1 through 3.

Table III. Some Distances (Å) and Angles (deg) Not Given in Figure 1

	Distances		
K–O(1)[a]	2.878 (3)	O(3)–H(1)	1.01 (8)
K–O(2)[a]	2.946 (3)	O(3)–H(2)	0.71 (5)
K–O(1)′	2.731 (3)	O(3)- - -S(1)	3.545 (4)
K–O(2)′	2.759 (3)	O(3)- - -S(2)	3.379 (4)
K–O(3)	2.843 (4)	H(1)- - -S(1)	2.619 (7)
K–O(3)′	2.875 (3)	H(2)- - -S(2)	2.692 (5)
	Angles		
O(1)–K–O(1)′	80.75 (6)	O(2)–K–O(2)′	72.97 (11)
O(1)–K–O(2)	66.89 (9)	O(2)–K–O(3)	150.88 (13)
O(1)–K–O(2)′	139.78 (11)	O(2)–K–O(3)′	127.69 (13)
O(1)–K–O(3)	141.09 (12)	O(2)–K–O(3)	78.39 (12)
O(1)–K–O(3)′	72.12 (11)	O(2)′–K–O(3)′	136.39 (13)
O(1)′–K–O(2)	128.53 (12)	O(3)–K–O(3)′	71.83 (10)
O(1)′–K–O(2)′	129.18 (11)	H(1)–O(3)–H(2)	92.8 (94)
O(1)′–K–O(3)	74.78 (10)	O(3)–H(1)–S(1)	151.8 (18)
O(1)′–K–O(3)′	72.21 (10)	O(3)–H(2)–S(2)	165.1 (11)

[a] These two oxygens are the ones shown in Figure 1 with the ligand.

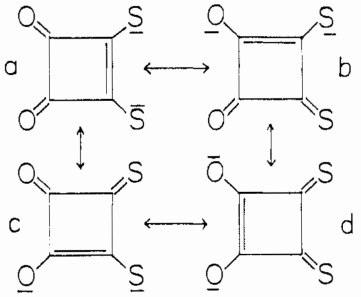

Figure 2. Resonance forms in the dithiosquarate dianion, $S_2C_4O_2{}^{2-}$.

Table IV. Comparison[a] of Selected Ligand Parameters in the Structures of the $Ni(Dts)_2{}^{2-}$ and $Cu_8(Dts)_6{}^{4-}$ Complexes

	$Ni(Dts)_2{}^{2-}$	$Cu_8(Dts)_6{}^{4-}$ [b]
C_1–C_2–C_3, deg	92.4 (3)	92.3 (16)
C_2–C_3–C_4, deg	87.9 (3)	87.6 (10)
C_3–C_4–C_1, deg	87.8 (3)	
C_4–C_1–C_2, deg	92.0 (3)	
S_2–C_2–C_3 (exo), deg	144.0 (2)	129.9 (14)
S_2–C_2–C_1 (endo), deg	123.6 (2)	137.8 (8)
S_1–C_1–C_4 (exo), deg	145.0 (2)	
S_1–C_1–C_2 (endo), deg	123.0 (2)	
S_1–S_2 ("bite"), Å	3.257 (2)	3.922 (14)
O–O, Å	3.210 (4)	3.292 (26)

[a] Esd's for the reported average interatomic distances and angles in the $Cu_8(Dts)_6{}^{4-}$ complex were computed as follows: $\sigma = [\Sigma_{i=1}{}^N(x_i - \bar{x})^2/(N-1)]^{1/2}$, where x_i is the length of the bond and $\bar{x}$ is the mean value for the N equivalent bond lengths.
[b] From ref 34.

apparent. However, the magnitudes of the S–C–C endo and exo angles are reversed in the two ligands. The S–S "bites" of 3.257 and 3.922 Å in the structures of the nickel and copper complexes, respectively, dramatically illustrate the remarkable flexibility of the dithiosquarate ligand. These values represent extreme deviations from the estimated[35] unstrained ligand bite of 3.75 Å.

The magnitude of the S–Ni–S intraligand angle of 94.19° is the largest observed for any of the Ni–S square chelate complexes. Average S–Ni–S angles in the dithiolenes, dithiophosphates, and 1,1-dithio complexes are 91.5, 88.0, and 79.0°, respectively.[6] Average values for the S–S bites in the same order are 3.10, 3.10, and 2.80 Å.

The large (3.257 Å) bite of the coordinated dithiosquarate ligand without doubt determines the size of the S–Ni–S angle and the short (3.027 Å) interligand S–S distance.

Two, significantly different, Ni–S bonds are found in the structure. The reason for this difference is not readily apparent; however, their average value of 2.22 (1) Å is similar to that found in the structures of the dithiophosphate and dithiophsophinate square complexes of nickel(II) (2.23–2.24 Å).[6]

The average value of the C–S bonds (1.691 (4) Å) is close to that observed in thiourea[36] and thiourea complexes.[37] The multiple character of the S–C bond is additional evidence for the importance of resonance forms b and c (Figure 2) in the description of the electronic structure of the ligand.

The potassium ions lie in the center of an irregular polyhedron defined by six oxygen atoms, two of which are contributed by the water molecules (Table IV).

(B) Synthesis and Characterization. The 1,2-dithiosquarate dianion was prepared from diethyl squarate which could be obtained either by reaction of perchlorocyclobutenone with ethanol in a modification of a procedure of Maahs[38] or by ethanol esterification of squaric acid.[39] On addition of diethyl squarate to sodium or potassium hydrosulfide in alcohol, the dithiosquarate salts are formed in high yields as bright yellow precipitates which can be recrystallized from aqueous ethanol or methanol. Sodium 1,2-dithiosquarate has also been prepared[1] in low yield (≤10%) from the bis(cyclohexylamide) of squaric acid, by the amide cleavage method of Shahak and Sasson.[40] The ir spectrum of the sodium salt shows two strong absorptions at 1710 and 1620 cm^{-1} and that of the potassium salt has absorptions at 1700 and 1625 cm^{-1} which can be attributed to C═O stretching vibrations. The electronic spectrum of the anion in aqueous solution shows peaks at 346, 325 (sh), 250, and 230 nm.

Reaction of potassium 1,2-dithiosquarate with ethyl iodide in DMF–water yields *S,S′*-diethyl 1,2-dithiosquarate. The ir spectrum (CCl4) shows strong bands at 1770, 1745, 1455, and 1135 cm^{-1}. The mass spectrum shows a strong parent ion peak at m/e 202, and the NMR spectrum is typical of S-bonded

Table V. Analytical Data and Physical Properties of the Ligand and Complexes

Complex	% C Calcd	% C Found	% H Calcd	% H Found	Color	Mp, °C	Conductivity,[a] $\mathrm{ohm^{-1}\,cm^{-1}}$
$K_2O_2C_4S_2\cdot H_2O$	19.99	19.89	0.84	0.89	Yellow		
$Na_2O_2C_4S_2\cdot 2.6H_2O$[b]	20.16	20.17	2.03	2.25	Yellow		
$K_2Mn(O_2C_4S_2)_2\cdot 4H_2O$	19.49	19.85	1.63	1.61	Yellow	*d*	505
$K_2Fe(O_2C_4S_2)_2\cdot 4H_2O$	19.43	19.18	1.63	1.24	Yellow	*d*	431
$K_2Co(O_2C_4S_2)_2$	20.82	20.57	0.87	0.49	Green	*d*	349
$K_2Ni(O_2C_4S_2)_2\cdot 2H_2O$	21.68	21.24	0.45	0.43	Red-brown	*d*	394
$K_2Zn(O_2C_4S_2)_2\cdot 2H_2O$	20.53	20.40	0.86	0.98	Yellow	*d*	292
$K_2Pd(O_2C_4S_2)_2\cdot 2H_2O$	18.88	18.84	0.79	0.73	Green	*d*	314
$K_2Pt(O_2C_4S_2)_2\cdot 2H_2O$	16.08	16.61	0.67	0.21	Red-brown	*d*	308
$(Ph_4P)_2Mn(O_2C_4S_2)_2$	65.81	65.28	3.95	3.87	Yellow	232 dec	286
$(Ph_4P)_2Fe(O_2C_4S_2)_2$	65.75	65.87	3.95	4.01	Yellow-brown	*d*	307
$(Ph_4P)_2Co(O_2C_4S_2)_2$	65.55	65.60	3.93	3.82	Green	215–217	359
$(Ph_4P)_2Ni(O_2C_4S_2)_2$	65.57	65.31	3.93	3.91	Brown	243–244	304
$(Ph_4P)_2Cu(O_2C_4S_2)_2$	65.26	65.88	3.91	3.95	Dark green	243–244	
$(Ph_4P)_2Zn(O_2C_4S_2)_2$	65.14	64.63	3.91	3.84	White	219–220	294
$(Ph_4P)_2Pd(O_2C_4S_2)_2$	62.65	62.47	3.76	3.58	Green	261–262	292
$(Ph_4P)_2Pt(O_2C_4S_2)_2$	57.87	57.61	3.47	3.35	Orange	285–295 dec	305
$(Ph_4P)_2Fe(O_2C_4S_2)_2\cdot 2EtOH$	64.63	64.97	4.70	4.88	Brown		
$(Ph_4P)_2Mn(O_2C_4S_2)_2\cdot 2EtOH$	63.56	63.00	4.19	4.17	Yellow		
$(Ph_4P)_2C_8O_4S_3$[c]	71.93	71.25	4.31	4.44	Amber	*d*	309

[a] Acetonitrile solutions (10^{-3} *M*) at 25° for Ph_4P^+ salts; water at 25° for K^+ salts. [b] Sulfur analysis: calcd, 26.92%; found, 26.81%. Oxygen analysis: calcd, 31.36%; found, 31.33%. [c] Phosphorus analysis: calcd, 6.62%; found, 6.44%. Sulfur analysis: calcd, 10.29%; found, 10.36%. [d] Decomposed over wide temperature range.

ethyl esters (δ 3.46 and 1.48 ppm with respect to TMS).

Anionic complexes of 1,2-dithiosquarate with transition metals can be formed by reaction with $1/n$ equiv of the n-valent metal cation.

Analytical data and physical properties of the complexes are shown in Table V. The syntheses of the complexes reported here are straightforward. Crystallization of the potassium salts begins immediately after concentrated aqueous solutions of the metal(II) salt and K_2Dts are mixed. Aqueous solutions of Fe(III) and Cu(II) are reduced by the ligand to Fe(II) and Cu(I), respectively. The iron(II) complex slowly decomposes in air.

Arylphosphonium salts of the tetrahedral complexes are insoluble in water and can be recrystallized from either DMF–water or acetonitrile–ether mixtures. Only the Mn(II) and Fe(II) complexes show a tendency to expand their coordination spheres by forming the solvates $(Ph_4P)_2M(Dts)_2\cdot 2S$ ($S = H_2O$, EtOH). The solvent molecules are not retained when these compounds are recrystallized from dry acetonitrile. The complexes are 2:1 electrolytes in acetonitrile solutions and can be classified in three structural groups on the basis of their composition and similarity of X-ray powder patterns (Table VI): the $(Ph_4P)_2M(Dts)_2\cdot 2S$ group (M = Mn(II), Fe(II); $S = H_2O$, isomorphous pair; $S = C_2H_5O$, isomorphous pair), the $(Ph_4P)_2M(Dts)_2$ group (M = Ni(II), Pd(II), Pt(II), Cu(II)), and the $(Ph_4P)_2M(Dts)_2$ group (M = Fe(II), Co(II), Zn(II)).

The Mn(II) complex, has a quite different X-ray powder pattern from those of the $(Ph_4P)_2M(Dts)_2$ complexes and a considerably more complex infrared spectrum. In the solid state all $(Ph_4P)_2M(Dts)_2$ complexes are air stable; however, solutions of the Co(II), Mn(II), and Fe(II) compounds decompose when exposed to air. This decomposition is quite rapid for the Mn(II) complex and occurs instantly with the Fe(II) compound.[41]

On prolonged standing in the air the final products obtained are insoluble metal-containing residues (which contain no Dts^{2-}) and the Ph_4P^+ salt of the monosulfide $(C_8O_4S_3)^{2-}$. The monosulfide can be extracted into and crystallized from CH_3CN. No monosulfide was obtained from the oxidation of the Co(II) compound, which instead afforded a dark green oily substance. The reluctance of this oil to crystallize resembles other such products obtained from reactions of Cr(III), Rh(III), and Ru(III) with Dts^{2-}.

Table VI. Representative X-Ray Powder Patterns of the Dithiosquarate Complexes[a,b]

$K_2O_2C_4S_2\cdot xH_2O$			$(Ph_4P)_2O_2C_4S_2$	
Ni	Zn	Mn	Zn	Ni
7.34 s	7.63 s	7.11 s	12.03 m	10.59 s
6.66 m	5.68 w	6.26 s	11.05 m	9.12 m
6.33 m	5.16 s	4.54 s	9.51 m	8.47 w
5.40 s	4.03 s	4.31 s	7.44 s	7.73 s
5.11 w	3.81 w	3.58 w	6.71 s	5.85 m
4.70 s	3.56 s	3.32 s	6.07 s	5.45 s
4.20 w	3.29 m	3.14 m	5.34 m	5.01 m
3.96 w	3.16 w	3.03 m	5.13 m	
3.79 w	3.02 s	2.92 m	4.72 m	4.65 s
3.65 w	2.88 s	2.80 m	4.52 s	4.36 s
3.38 s	2.55 s		3.99 s	4.17 m
3.25 s				

[a] The first 12 lines that could be measured are reported.
[b] The *d* spacings of all the reported complexes are available.[32]

The infrared spectra of the various complexes are quite similar (Table VII). However, there exist small variations in the energies of four groups of bands which seem to depend on the molecular geometry (tetrahedral vs. planar) of the complexes. Specifically, the multiplets of absorptions found in the ranges from 1830 to 1700 and from 1440 to 1340 $\mathrm{cm^{-1}}$ consistently occur at higher frequencies in the planar complexes. These are to be contrasted with absorptions in the 1170–1150- and 895–870-$\mathrm{cm^{-1}}$ regions which are found at lower energies in the planar complexes.

The larger (unstrained) bite and the more extensive electron delocalization in the ligands of the tetrahedral complexes, suggest that resonance forms b, c, and d (Figure 2) are more important in these complexes than in the planar complexes. Consistent with this suggestion are the observed systematic variations in the infrared spectra. These variations can be rationalized if the absorptions in the 1830–1700 and 1440–1340-$\mathrm{cm^{-1}}$ regions are assigned to $\mathrm{C\overset{\cdots}{-}O}$ and $\mathrm{C\overset{\cdots}{-}C\overset{\cdots}{-}O}$ vibrations. The remaining two groups of absorptions at 1170–1150 and 895–870 $\mathrm{cm^{-1}}$ similarly can be assigned to the $\mathrm{C\overset{\cdots}{-}C\overset{\cdots}{-}S}$ and $\mathrm{C\overset{\cdots}{-}S}$ vibrational frequencies, respectively.

(C) Electronic and Structural Properties. (1) Planar Complexes. The stoichiometry, magnetic properties (Table VIII), and the isomorphism of the $(Ph_4P)_2M(Dts)_2$ complexes (M = Cu(II), Ni(II), Pd(II), Pt(II)) leave little doubt that these molecules are four-coordinate square complexes. The

Table VII. Representative Vibrational Spectra[a,c]

Complexes	Tentative assignments[b]			
	$\mathrm{C}\overset{\cdots}{-}\mathrm{O}$	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{O}$	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{S}$	$\mathrm{C}\overset{\cdots}{-}\mathrm{S}$
$(\mathrm{Ph_4P})_2\mathrm{Mn}(\mathrm{O_2C_4S_2})_2\cdot 2\mathrm{H_2O}$	1720 s, 1680 s, 1665 s, 1645 s	1370 s, sh, 1345 s, 1340 sh	1200 sh, 1190 s, b, 1170 sh	995 m, 905 m, 895 m
$(\mathrm{Ph_4P})_2\mathrm{Fe}(\mathrm{O_2C_4S_2})_2\cdot 2\mathrm{H_2O}$	1720 s, 1680 s, 1665 s, 1640 s	1370 sh, 1355 s	1200 sh, 1185 s, b, 1170 sh	995 m, 900 m, 890 m
$(\mathrm{Ph_4P})_2\mathrm{Mn}(\mathrm{O_2C_4S_2})_2\cdot 2\mathrm{EtOH}$	1832 m, 1725 s, 1690 s, 1660 m	1385 s, 1362 s	1175 s, 1165 sh	1040 m, 992 m, 915 m, 888 m, 875 sh
$(\mathrm{Ph_4P})_2\mathrm{Fe}(\mathrm{O_2C_4S_2})_2$	1815 w, 1720 s, 1700 s, 1660 sh	1390 s, 1365 s	1175 s, 1160 sh	1045 m, 990 m, 910 m, 882 m, 875 m
$(\mathrm{Ph_4P})_2\mathrm{Ni}(\mathrm{O_2C_4S_2})_2$	1825 w, 1730 s, 1700 s, 1650 sh	1425 s	1160 s	1000 m, 910 m, 870 m, 860 m
$\mathrm{K_2Mn}(\mathrm{O_2C_4S_2})_2\cdot 4\mathrm{H_2O}$	1900 w, 1730 s, b, 1650 s, b	1420 m, 1360 s, b	1215 s, b, 1120 m	950 m, 915 s
$\mathrm{K_2Fe}(\mathrm{O_2C_4S_2})_2\cdot 4\mathrm{H_2O}$	1900 w, 1730 s, b, 1640 s, b	1415 m, 1360 s, b	1215 s, b, 1120 m	950 m, 910 s
$\mathrm{K_2Ni}(\mathrm{O_2C_4S_2})_2\cdot 2\mathrm{H_2O}$	1875 m, 1735 s, b, 1690 s, 1670 s	1415 s, b	1180 s, 1130 w	935 m, 880 m

[a] Frequencies reported in cm^{-1}: s, strong; w, weak; m, medium; sh, shoulder; b, broad. Near-infrared spectra were taken in Nujol mulls between NaCl plates. [b] Absorptions attributed to noninteracting cations are not included in the table. [c] A complete list of infrared spectra for all the reported complexes is available.[32]

visible spectra of these compounds (Table VIII) suggest that the planar structures are retained in solution. It is quite remarkable that in the solid state the structure of the $\mathrm{K_2Ni(Dts)_2\cdot 2H_2O}$ complex is strictly four-coordinate and planar. It seems likely that the ligand field stabilization of the planar form compensates for the energetically unfavorable distortion obvious in the structure of the Dts ligand. The only example of tetrahedral $\mathrm{NiS_4}$ to date is found in the structure of the bis(imidodithiophosphinato)nickel(II) complex cation. The average bite size of the neutral imidodithiophosphinate ligand (ca. 3.55 Å) in the complex is close to the value expected for the dithiosquarate dianion.

The relative energies of the d–d transitions in the dithiosquarate complexes of Cu(II), Ni(II), and Pd(II) (Table VIII) parallel those observed in the corresponding $\mathrm{M(Mnt)_2}^{2-}$ complexes.[4] The $^1\mathrm{A_g} \rightarrow {}^1\mathrm{B_{1g}}$ (D_{2h} symmetry) transition in the nickel complex at 12,000 cm^{-1} is very similar to the one observed in the spectrum of the $\mathrm{Ni(Mnt)_2}^{2-}$ complex.[4] Correcting the energy separation ($\mathrm{d}_{x^2-y^2} - \mathrm{d}_{xy}$) for electron repulsions and assuming a reasonable value for the Slater–Condon parameters,[42] the parameter Δ_1 (which reflects the ligand field strength[43]) of the dithiosquarate ligand is calculated to be 14,800 cm^{-1}. A comparison of the Δ_1 value for the $\mathrm{Ni(Dts)_2}^{2-}$ complex to values of the same parameter reported[44] for other sulfur complexes, places the Dts ligand among the weaker sulfur chelates. Formally the Dts ligand can be classified with the 1,2-dithiolate ligands. However, contrary to what is observed with $\mathrm{Ni(Mnt)_2}^{2-}$, the $\mathrm{Ni(Dts)_2}^{2-}$ complex does not oxidize or reduce reversibly. This lack of redox properties perhaps reflects the effect of the large "bite" of the Dts ligand. It is interesting that $\mathrm{M(Dts)_2}^{n-}$ complexes of metal ions, other than first row (and larger ionic radii), exhibit reversible redox behavior[45] (Figure 3).

(2) Tetrahedral Complexes. The $\mathrm{Ph_4P^+}$ salt of the $\mathrm{Co(Dts)_2}^{2-}$ complex is a green crystalline solid with a powder pattern and infrared spectrum virtually identical with those of $\mathrm{Ph_4P^+}$ "salts" of the $\mathrm{Fe(Dts)_2}^{2-}$ and $\mathrm{Zn(Dts)_2}^{2-}$ complexes (Tables VI, VII). The solid-state magnetic moment (4.69 BM) is comparable to moments observed[10] in other tetrahedral high-spin Co(II) complexes (4.68 BM for $[((\mathrm{CH_3})_2\mathrm{PS})\mathrm{N}]_2\mathrm{Co^{II}}$ and 4.56 BM for $[((\mathrm{C_6H_5})_2\mathrm{PS})\mathrm{N}]_2\mathrm{Co^{II}}$); however, it is considerably lower than the abnormally high moment reported[8] for the $(\mathrm{F_2PS_2})_2\mathrm{Co^{II}}$ complex (6.2 BM).

The near-infrared spectra of the $\mathrm{Fe^{II}}$– and $\mathrm{Co^{II}}$–Dts complexes (Figure 4) are compared to those of other tetrahedral sulfur chelates in Table IX. In both complexes Δt is larger than the value reported for the analogous complexes

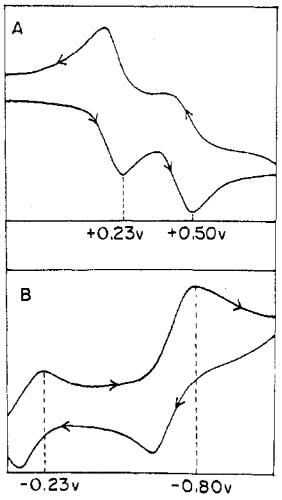

Figure 3. Cyclic voltammetry of dithiosquarate complexes: (A) oxidation of the $[\mathrm{Pt(S_2C_4O_2)_2}]^{2-}$ complex; (B) reduction of the $[\mathrm{Au(S_2C_4O_2)_2}]^{-}$ complex. Also shown are the oxidation of $\mathrm{Ni(Mnt)_2}^{2-}$ (0.23 V) and the reduction of $\mathrm{Ni(Mnt)_2}^{-}$ (−0.23 V) both used as internal standards. The values of the potentials were unaffected by the presence of the internal standards.

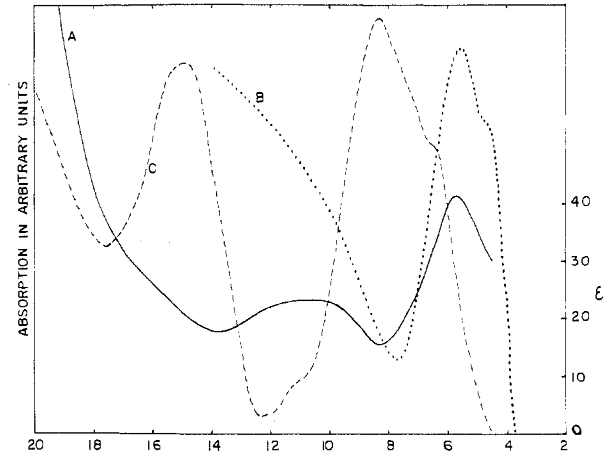

Figure 4. Near-infrared–visible spectra: (A) $\mathrm{Fe(Dts)_2}^{2-}$, 0.0165 *M* $\mathrm{CH_3CN}$ solution; (B) $\mathrm{Fe(Dts)_2}^{2-}$ reflectance spectrum; (C) $\mathrm{Co(Dts)_2}^{2-}$ reflectance spectrum. The absorption centered at 11 kK in spectrum A reflects the presence of a minute amount of oxidized $\mathrm{Fe(Dts)_2}^{2-}$ which is characterized by a very intense charge-transfer absorption in that region.

Table VIII. Electronic Spectra

Compd	Reflectance	Solution[a]	Assignment[b]	$\mu_{\mathrm{eff}}^{\mathrm{cor},c}$ BM
$K_2Mn(O_2C_4S_2)_2 \cdot 4H_2O$		29,410 (38,500)		6.13
		31,250 sh (31,000)		
		40,820 (22,000)		
$(Ph_4P)_2Mn(O_2C_4S_2)_2$		32,260 b (38,180)		5.87
		36,360* (30,960)		
		44,440 (86,700)		
$K_2Fe(O_2C_4S_2)_2 \cdot 4H_2O$	8,330 sh	29,590 (39,000)	$^5T_{2g} \rightarrow {}^5E_g$(oct)	5.00
	10,500	31,250 sh (34,000)		
		40,820 (22,000)		
$(Ph_4P)_2Fe(O_2C_4S_2)_2$	4,800 sh	5,800 (41)	$^5E \rightarrow {}^5T_2$(tet)	4.83
	5,550	25,000 sh (4650)		
		32,790 (39,500)		
		37,940* (27,910)		
		44,440 sh (93,020)		
$K_2Co(O_2C_4S_2)_2 \cdot 2H_2O$	8,060	8,300 (34)	$^4A_2 \rightarrow {}^4T_1$(F)(tet)	4.60
	14,900	31,250 b (34,000)	$^4A_2 \rightarrow {}^4T_1$(P)	
		40,000 (21,000)		
$(Ph_4P)_2Co(O_2C_4S_2)_2$	8,300	8,300 (136)	$^4A_2 \rightarrow {}^4T_1$(F)	4.69
	14,700	15,100 (281)	$^4A_2 \rightarrow {}^4T_1$(P)	
		23,530 sh (3920)		
		30,770 sh (33,300)		
		32,790 (47,000)		
		36,360* (26,470)		
		43,480 (73,500)		
$K_2Ni(O_2C_4S_2)_2 \cdot 2H_2O$		12,000 (43)	$^1A_g \rightarrow {}^1B_{1g}$(pl)	Diamag
		16,660 sh (74)		
		26,320 sh (14,000)		
		29,670 sh (30,000)		
		32,050 (47,500)		
		40,000 (30,500)		
$(Ph_4P)_2Ni(O_2C_4S_2)_2$		12,000 (44)	$^1A_g \rightarrow {}^1B_{1g}$(pl)	Diamag
		16,660 sh (78)		
		26,320 (17,720)		
		32,260 (44,300)		
		37,740* (31,640)		
		44,440 sh (83,500)		
$(Ph_4P)_2Cu(O_2C_4S_2)_2$		9,175 (159)		1
		25,640 (7930)		
		31,250 (32,840)		
		32,260 sh (29,450)		
		39,220 (23,780)		
		44,440 sh (75,900)		
$K_2Pd(O_2C_4S_2)_2$		16,130 (108)		Diamag
		28,570 (21,500)		
		35,090 (38,000)		
$(Ph_4P)_2Pd(O_2C_4S_2)_2$		16,130 (107)		Diamag
		28,570 (48,530)		
		36,360 (73,530)		
		44,440 (131,000)		
$K_2Pt(O_2C_4S_2)_2$		25,770 (20,050)		Diamag
		37,310 (31,000)		
		44,640 (40,000)		
$(Ph_4P)_2Pt(O_2C_4S_2)_2$		26,320 b (19,830)		Diamag
		32,260 sh (17,000)		
		37,740* (34,000)		
		43,480 (114,700)		
$(Ph_4P)_2O_2C_4S_2$		27,780 (29,000)		
		30,300 sh (21,000)		
		37,740 (21,000)		
		45,450 sh (81,000)		
$(Ph_4P)_2C_8O_4S_3$		26,000 (15,000)		
		31,750 (28,000)		
		44,440 sh (84,000)		

[a] Spectra of aqueous solutions of the potassium salts and CH_3CN solutions of the Ph_4P^+ salts are reported; asterisked absorptions represent the center of a phenyl ring doublet and variations in intensities are attributed to underlying charge-transfer bands. [b] The assumed stereochemistry is given parentheses. [c] Estimated uncertainty in the magnetic measurements ±0.05 BM.

with the dodecapeptide (Boc-(Gly-L-Cys-Gly)$_4$-NH_2)$^{2-}$ and the $[(R_2PS)_2N]_2M$ complexes (R = CH_3, C_6H_5; M = Co(II), Ni(II)). The electronic d–d transitions in the $Fe(Dts)_2{}^{2-}$ complex (4800 and 5550 cm^{-1}), however, are of lower energies than the corresponding transitions in reduced rubredoxin (6000 and 4700 cm^{-1}).[48] The infrared spectra and powder pattern of the Mn(II) complex are different from those observed for either the planar complexes or the Co(II), Fe(II), and Zn(II) complexes. The magnetic moments 5.87 and 6.13 BM for the Ph_4P^+ and K^+ salts, respectively, are similar to values reported for the bis(difluorodithiophosphate)[8] complex (5.9 BM) and the bis(imidodithiophosphinate) complex (5.75 BM). The structure of the latter complex has been reported and is tetrahedral.[13]

The physical properties of the $M(Dts)_2{}^{2-}$ complexes (M = Zn(II), Co(II), Fe(II)) leave little doubt that in these mol-

Table IX. Summary of Spectral Data for Selected Tetrahedral Sulfur Chelates (cm^{-1})

Complex	ν_2	ν_3	Δt	B'	Ref
$[((CH_3)_2PS)_2N]_2Co$	6576	14,399	3831	632	10
$[Co(Boc\text{-}(Gly\text{-}L\text{-}Cys\text{-}Gly)_4\text{-}NH_2)]^{2-}$	6539	14,974	4295	636	16
$Co(Dts)_2{}^{2-}$	8300^a	14,700^a (15,100)^b	~5330	~510	
$[((CH_3)_2PS)_2N]_2Fe$		3,500			10
$[Fe(Boc\text{-}Gly\text{-}L\text{-}Cys\text{-}Gly)_4\text{-}NH_2)]^{2-}$		5,100			16
$Fe(Dts)_2{}^{2-}$	4800 sh^a	5,550^a (5,800)^b			
Iron(II) rubredoxin	6000	7,400			48

^{a} Reflectance spectra. ^{b} CH_3CN solution spectra.

ecules the metal ions are tetrahedrally coordinated both in solution and in the solid state. Tetrahedrally coordinated, monomeric Fe(II) complexes with sulfur chelating ligands have been isolated previously[10] with the bis(imidodithiophosphinate) ligands. Unfortunately, these complexes do not undergo oxidation, and their utility as analogs for the active site of rubredoxin is limited. The same situation prevails with the $Fe(Dts)_2{}^{2-}$ complex, which oxidizes irreversibly, to afford ligand-derived monosulfides or (in the presence of halide ions) five-coordinate complexes of the type $[Fe^{III}(Dts)_2X]^{2-}$.[41]

For idealized tetrahedral geometry and Fe^{III}–S bond lengths of 2.3 Å (similar to the three "long" bonds in the structure of the oxidized rubredoxin[48]) an S–S bite of 3.75 Å is required. This is precisely the value calculated for the unstrained Dts ligand.[35] The apparent instability of an $Fe^{III}(Dts)_2{}^-$ complex probably derives from electronic rather than steric reasons. It is worth emphasizing, however, that even with a dodecapeptide ligand that presumably simulates the coordination environment of the iron in rubredoxin, reversible oxidation does not seem to be a facile process.[16] The stability of the $Fe^{III}S_4$ chromophore in oxidized rubredoxin may be associated with the unique (2.05 ± 0.03 Å) Fe–S bond.[48] A shortening of the M–S bond has been observed upon oxidation of certain sulfur chelates and has been attributed to covalency.[49]

Conclusions

The dithiosquarate ligand is formally analogous, and its complexes were predicted[50] to possess properties similar to the 1,2-dithiolene complexes. From the properties of the bivalent, first-row dithiosquarate–metal complexes the following radical differences are apparent: (a) no reversible redox properties are observed with the $M(Dts)_2{}^{2-}$ complexes in marked contrast to the 1,2-dithiolene complexes; (b) tetrahedral structures that are rarely (if ever!) found with the 1,2-dithiolene ligands seem to be rather common with the dithiosquarate ligand; (c) low oxidation states are favored with the dithiosquarate complexes, while 1,2-dithiolenes and 1,1-dithio complexes are noted for their ability to stabilize metal ions in high formal oxidation states.

The origin of these differences is essentially the unusually large S–S "bite" of the dithiosquarate ligand. A large S–S "bite" favors tetrahedral geometry and the larger ionic radii of low-valent metal ions and/or high-spin configurations. A final comment should be made concerning ligands with extended electronic delocalization properties. An unsaturated ligand π system is not necessarily a sufficient condition for strong metal–ligand π bonding in sulfur chelates. The energies of the ligand π orbitals relative to those of metal orbitals of appropriate symmetry also must be adequately matched for overlap and π bonding to occur.

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Registry No. Diethyl squarate, 5231-87-8; perchlorocyclobutenone, 2892-63-9; K_2Dts, 52427-61-9; $(Ph_4P)_2Dts$, 56487-98-0; $K_2Mn(Dts)_2\cdot4H_2O$, 56488-47-2; $K_2Fe(Dts)_2$, 56488-48-3; $K_2Co(Dts)_2$, 56488-49-4; $K_2Ni(Dts)_2\cdot2H_2O$, 52646-84-1; $K_2Zn(Dts)_2\cdot2H_2O$, 56488-50-7; $K_2Pd(Dts)_2$, 56488-51-8; $K_2Pt(Dts)_2$, 56488-52-9; $(Ph_4P)_2Co(Dts)_2$, 56488-54-1; $(Ph_4P)_2Ni(Dts)_2$, 56488-56-3; $(Ph_4P)_2Zn(Dts)_2$, 56488-33-6; $(Ph_4P)_2Pd(Dts)_2$, 56488-35-8; $(Ph_4P)_2Pt(Dts)_2$, 56488-37-0; $(Ph_4P)_2Cu(Dts)_2$, 56498-50-1; $(Ph_4P)_2Fe(Dts)_2$, 56488-39-2; $(Ph_4P)_2Mn(Dts)_2$, 56488-41-6; $Na_2O_2C_4S_2$, 52427-60-8.

Supplementary Material Available. A listing of structure factor amplitudes plus tables of additional X-ray powder patterns and vibrational spectra will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50411I-11-75.

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Contribution from Gilman Hall and Ames Laboratory—ERDA,
Iowa State University, Ames, Iowa 50010

Crystal and Molecular Structure of Bromotetrakis(trimethyl phosphito)nickel(II) Tetrafluoroborate, $\{Ni[P(OCH_3)_3]_4Br\}BF_4$

D. S. MILBRATH, J. P. SPRINGER, J. C. CLARDY,[1] and J. G. VERKADE*

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The crystal and molecular structure of the five-coordinate nickel complex $\{NiBr[P(OCH_3)_3]_4\}BF_4$ has been determined from three-dimensional single-crystal X-ray data. The compound crystallizes in the monoclinic space group $P2_1/n$, with $a = 13.333$ (4), $b = 18.195$ (5), $c = 11.731$ (2) Å, and $\beta = 93.61$ (2)°. The structure was determined by Patterson and conventional least-squares methods using 2894 independent nonzero reflections to give a final R factor of 0.060. The coordination geometry around Ni is essentially trigonal bipyramidal with Br in an equatorial position. Axial Ni–P distances are 2.181 (2) and 2.180 (2) Å while the equatorial Ni–P bonds are 2.187 (2) and 2.239 (2) Å and the Ni–Br distance is 2.456 (2) Å. The equatorial plane angles are Br–Ni–P = 123.44 (7) and 112.24 (7)°, and the P–Ni–P angle is 124.31 (9)°. The axial phosphorus ligands are bent toward the bromine with an average angle of 86.12°. Qualitative bonding considerations are used in comparing the present structure to others in the low-spin NiL_5^{2+}, NiL_4X^+, and NiL_3X_2 series.

Introduction

Few structural determinations of five-coordinate low-spin monodentate nickel(II) complexes in the series NiL_5^{2+}, NiL_4X, NiL_3X_2 (X = halogen or pseudohalogen) appear in the literature. The only NiL_5^{2+} example for which structural data have been obtained is that in which L is the adamantane-like caged phosphite $P(OCH)_3(CH_2)_3$.[2] The relatively undistorted trigonal-bipyramidal geometry of this complex appears to persist in solution since the ^{31}P NMR spectrum for the close analog $Ni[P(OCH_2)_3CCH_3]_5^{2+}$ shows an A_3B_2 pattern at low temperature.[3] Earlier spectral assignments of trans cyano configurations in $Ni[P(OR)_3]_3(CN)_2$[4] and $Ni[P(OR)_2C_6H_5]_3(CN)_2$[5] were later supported by X-ray diffraction studies of $Ni[P(OC_2H_5)_2C_6H_5]_3(CN)_2$[6] and $Ni[P(CH_3)_2C_6H_5]_3(CN)_2$[7] although the geometries in both cases were somewhat distorted from trigonal bipyramidal. The conclusion drawn from one electronic study[8] that the halogens in $Ni[P(CH_3)_3]_3Br_2$ were trans was at variance with the suggestion based on a similar investigation in another laboratory[9] that they were cis. The question was resolved recently, however, by an X-ray diffraction study in which it was shown that the bromines lie in the equatorial plane of a trigonal bipyramid.[10] The same technique yielded similar geometries for $Ni[PH(C_6H_5)_2]_3I_2$[11] and $Ni[P(OCH_3)_3]_3I_2$[12] although both trigonal-bipyramidal and tetragonal-pyramidal coordination was observed in $NiL_3(CN)_2$ (L = 5-methyl-5*H*-dibenzophosphole), depending on the recrystallizing solvent.[13]

Aside from the distorted tetragonal-pyramidal structures found for some high-spin divalent iron, cobalt, and nickel complexes of the type $[ML_4X]^+$, where L = $OP(C_6H_5)_3$, $OAs(C_6H_5)_3$, $OP(C_6H_5)_2CH_3$, and $OAs(C_6H_5)_2CH_3$ and X = ClO_4,[14,15] no structures have been reported for low-spin members of this class. The low-spin cation in $Ni[PH(CH_2CH_3)_2]_4X[B(C_6H_5)_4]$ (X = Cl, Br, I, NCS)[16] and the isoelectronic complexes $\{Co[PF_2(C_6H_5)]_4X\}$, X = Cl, Br,[17] have been tentatively assigned tetragonal-pyramidal structures on the basis of electronic, infrared, and, additionally in the latter compound, ^{31}P and ^{19}F NMR spectral studies. The present ambiguity of such techniques for purposes of structural assignment in these systems coupled with the subtle forces which determine their stereochemistries prompted us to carry out an X-ray structural determination of $\{Ni[P(OCH_3)_3]_4Br\}BF_4$, a low-spin member of the ML_4X^+ class.

Collection and Reduction of X-Ray Data

The compound $\{NiBr(P(OCH_3)_3)_4\}BF_4$ was prepared by a procedure to be described elsewhere[18] and was recrystallized in a closed container by vapor diffusion of ether into a concentrated acetone solution. The deep red crystal selected for data collection was mounted in a 0.3-mm sealed Lindemann capillary to overcome the problem of sensitivity of the compound to prolonged exposure to atmospheric conditions. The crystal used was a rectangular column measuring 0.20 × 0.28 × 0.34 mm.

Data were collected at room temperature using a Syntex $P2_1$ automated four circle diffractometer operating with graphite-monochromated Cu Kα radiation (λ 1.5418 Å). The unit cell was determined to be monoclinic, $a = 13.333$ (4), $b = 18.195$ (5), $c = 11.731$ (2) Å, and $\beta = 93.61$ (2)°, using standard crystallographic techniques.

A density of 1.690 g/cm^3 was computed from the cell volume of 2840.2 Å^3 on the basis of four $\{NiBr[P(OCH_3)_3]_4\}BF_4$ ion pairs per unit cell. This agrees well with a density of 1.69 g/cm^3 measured by flotation using n-C_7H_{16}–$BrCH_2CH_2Br$ mixtures.

Data were taken with a variable ω-scan mode at a minimum scan rate of 3°/min within a 2θ sphere of 114° ($(\sin\theta)/\lambda = 0.544$ Å^{-1}). During data collection, intensities of three standards $(40\bar{4})$, $(52\bar{3})$, and $(60\bar{2})$ were monitored after every 50 reflections. The intensities of these standards decreased by 15% during the measurement of two octants (4434 reflections).

The collected data were scaled for decomposition using the al-