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Neutron Diffraction Study of the Structure of Zeise's Salt, $\text{KPtCl}_3(\text{C}_2\text{H}_4)\cdot\text{H}_2\text{O}^1$

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The molecular structure of Zeise's salt, $\text{KPt}(\text{C}_2\text{H}_4)\text{Cl}_3\cdot\text{H}_2\text{O}$, has been studied by single-crystal neutron diffraction techniques. The PtCl_3 moiety forms a nearly planar group with the platinum atom 0.03 Å from the least-squares plane through the PtCl_3 group. The Pt-Cl bond trans to the ethylene group [2.340 (2) Å] is significantly longer than the cis Pt-Cl bonds [2.302 (2) and 2.303 (2) Å]. This difference, which is 19 times its standard deviation, is probably attributable to the trans-directing influence of the ethylene ligand. The carbon atoms are approximately equidistant from the platinum atom [2.128 (3) and 2.135 (3) Å], and the distance from the midpoint of the C-C bond to the platinum atom is 2.022 Å. The C-C distance, 1.375 (4) Å, is 0.038 Å longer than the value found in free ethylene, indicating some $d\pi-p\pi^*$ back-bonding from the platinum atom to C_2H_4 . Back-bonding is also indicated by a bending of the four hydrogen atoms away from the platinum atom: the carbon atoms are at an average distance of 0.164 Å from the plane of the four hydrogen atoms, and the angle between the normals to the methylene planes (the α angle) is 32.5°. Both the magnitude of α and the C-C bond lengthening are considerably smaller in Zeise's salt than in metal complexes of C_2F_4 and $\text{C}_2(\text{CN})_4$, suggesting that the amount of metal-ligand back-bonding may be greater in these complexes than in those involving ethylene. Crystallographic details: space group $P2_1/c$, with $a = 11.212$ Å, $b = 8.424$ Å, $c = 9.696$ Å, $\beta = 107.52^\circ$, $V = 873.4$ Å³, and $Z = 4$. Data were collected using a θ - 2θ step-scan procedure with neutrons of wavelength λ 1.021 Å at the Brookhaven high-flux beam reactor. The final agreement factor R (based on F) for the 1210 reflections with $I > 3\sigma(I)$ is 0.070.

Introduction

In 1825, William Zeise set into reflux a mixture of PtCl_4 and PtCl_2 in ethyl alcohol, treated the resultant black solid with KCl and HCl, and isolated cream-lemon crystals.³ The report of the crystals' composition, $\text{KPtCl}_3(\text{C}_2\text{H}_4)\cdot\text{H}_2\text{O}$, immediately ignited a lengthy controversy between Zeise and Liebig, who believed that the salt contained an intact ethoxy moiety.⁴ Accepted proof of Zeise's formulation came 13 years later when Birnbaum isolated the complex from a solution of platonic acid, $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$, treated with ethylene.⁵

Zeise's platinum-ethylene complex, later referred to as Zeise's salt in the literature, was the first organometallic compound to be isolated in pure form. This discovery spawned a tremendous growth in organometallic chemistry⁶ and still serves as the simplest example of transition metal-olefin complexation.

Zeise's salt has become one of the most cited examples of the Dewar-Chatto-Duncanson model for metal-olefin complexation^{7,8} where a σ bond is formed by overlap of the π orbital of the olefin with a $5d\sigma 6p^2$ hybrid orbital of the platinum atom, and a π back-bond is formed by overlap of a filled $5d\pi$ orbital with the antibonding π^* orbital of the olefin. Although the gross features of this model are now generally accepted, there is still some disagreement on the relative importance of the π back-bonding in stabilizing the platinum-ethylene interaction.

Both X-ray photoelectron spectroscopic⁹ and ³⁵Cl nuclear quadrupole resonance¹⁰ studies on Zeise's salt indicate considerable back-donation to the olefin in agreement with the Dewar-Chatto-Duncanson model. They also show electron shift to the trans chlorine atom relative to the cis chlorine atoms which is consistent with the trans influence of ethylene. These studies then imply that $d\pi-p\pi^*$ back-bonding is important. On the other hand, nuclear magnetic resonance¹¹ and neutron inelastic scattering¹² experiments indicate that the

coordinated ethylene undergoes a large-amplitude rotational oscillation, an observation which appears to argue against the presence of strong $d\pi-p\pi^*$ bonding. Various molecular orbital calculations¹³⁻¹⁵ give different estimates of the relative strength of $d\pi-p\pi^*$ back-bonding.

It has been realized for some time that a knowledge of the detailed structure of Zeise's salt would be useful in resolving some of the questions regarding the bonding in this compound. If $d\pi-p\pi^*$ back-bonding were important, the ethylene π^* orbitals would become partially occupied. This would in turn lead to (a) a lengthening of the C-C bond and (b) a loss of planarity of the ethylene molecule, as the carbon atoms assume some sp^3 character.

In 1953, Wunderlich and Mellor reported the first X-ray study of Zeise's salt.¹⁶ Their study assumed space group $P2_1$, and the structure was solved from two Patterson projections (010, 001) and a single electron density projection (010). Their data were only sufficient to locate the positions of the PtCl_3 moiety and the potassium cation. Later they published an improved study in which the ethylene carbon atoms were located and the trans Pt-Cl bond was determined to be abnormally long.¹⁷ Bokii and Kukina in 1957 recollected data on Zeise's salt by the precession method as part of a study on divalent haloplatinum complexes.¹⁸ Again, data were limited to two-dimensional projections, and the space group was assumed to be $P2_1$. These early studies on Zeise's salt supported Chatt's thesis that the ethylenic C-C bond in the complex is perpendicular to the PtCl_3 plane.⁸

In 1969, Black, Mais, and Owston reported the first three-dimensional X-ray structural determination of Zeise's salt.¹⁹ Their results showed that the trans influence of the ethylene was not as large as previously described. Also in 1969, Hamilton, Klanderma, and Spratley reported a neutron diffraction study of Zeise's salt in space group $P2_1$.²⁰ In this latter study, the hydrogen atoms were located and found to

Table I. Crystal Data for $\text{KPtCl}_3(\text{C}_2\text{H}_4)\cdot\text{H}_2\text{O}^{21}$

Space group $P2_1/c$	$\beta = 107.52 (4)^\circ$
$Z = 4$	$V = 873.4 \text{ \AA}^3$
Mol wt 386.6	$\rho(\text{calcd}) = 2.95 \text{ g/cm}^3$
$a = 11.212 (3) \text{ \AA}$	$\mu = 1.025 \text{ cm}^{-1}$ (for $\lambda 1.0 \text{ \AA}$ neutrons)
$b = 8.424 (6) \text{ \AA}$	
$c = 9.696 (6) \text{ \AA}$	

be bent away from the platinum atom. However, the refinement indicated relatively large standard deviations in the observed atomic parameters and unusually large temperature factors for the cis chlorine atoms. These large uncertainties were originally attributed to poor crystal quality and high thermal motion, but it is now apparent that a misassignment of the space group was almost certainly responsible.

Jarvis, Kilbourn, and Owston inferred in 1970 that the space group of Zeise's salt had been misassigned, when attempts to refine the structure with the effects of anomalous dispersion taken into account failed to yield improved results.²¹ Long exposure of upper layer photographs of the type hnl ($n = 1, 2, 3, \dots$) revealed a doubling of the c axis and the existence of a c glide plane perpendicular to the b axis. The real space group was therefore found to be $P2_1/c$ with the c axis twice as long as the original c axis in $P2_1$. When the data were recollected and analyzed in the correct space group, significantly different parameters for the $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ complex were obtained. The C-C bond length [$1.37 (3) \text{ \AA}$] was found to be only slightly longer than the C-C distance in uncomplexed ethylene [$1.337 (2) \text{ \AA}$]²² and the disparity between cis and trans Pt-Cl bond lengths [$2.305 (7)$ vs. $2.327 (5) \text{ \AA}$] was smaller than previously observed.

The present three-dimensional neutron diffraction investigation has been undertaken in order to allow an improved appraisal of the bonding in Zeise's salt. Primary emphasis has been placed upon the determination of (i) the degree to which the ethylene hydrogen atoms are bent away from the metal atom, (ii) an accurate estimate of the carbon-carbon bond length of the coordinated ethylene molecule, and (iii) a description of the hydrogen-bonding network in the crystalline state.

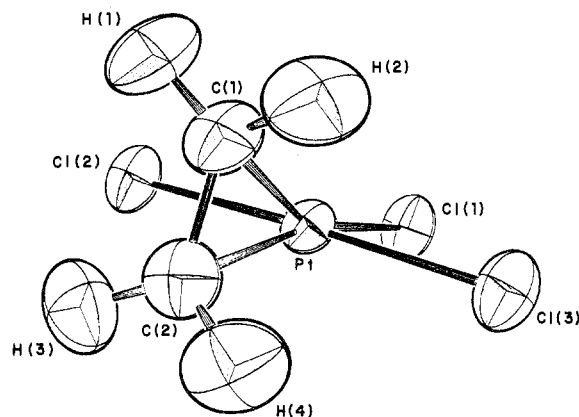
Experimental Section

Data Collection A suitable crystal of $\text{KPtCl}_3(\text{C}_2\text{H}_4)\cdot\text{H}_2\text{O}$ measuring approximately $6 \times 1.5 \times 1.5 \text{ mm}$ (volume 8.51 mm^3) was selected from a commercial sample supplied by Alfa Inorganics. The crystal was assigned along the 104 reciprocal axis for data collection. Data were collected at the Brookhaven National Laboratory high-flux beam reactor²³ with a θ - 2θ scan technique and a neutron wavelength $\lambda 1.021 \text{ \AA}$. One asymmetric unit of data was collected within a d^* limit of 1.25 \AA^{-1} in two stages: low-angle data ($0.00 < d^* < 0.50$) were collected with a scanning formula $\Delta 2\theta = 3.20 (1 - 0.41 \tan \theta)$ and high-angle data ($0.50 < d^* < 1.25$) with $\Delta 2\theta = 1.50 (1 + 5.30 \tan \theta)$. Each reflection was scanned from high to low 2θ in approximately 40 steps. Throughout data collection a pair of reflections (502 and 042 for the low-angle data set and 540 and 444 for the high-angle data set) were periodically monitored for any changes in intensity. No significant changes were observed.

Background corrections were made with a method which divides the reflection profile in such a way that $\sigma(I)/I$ is minimized.²⁴ The observed intensities were corrected for Lorentz effects. An absorption correction was applied by numerical integration over a gaussian grid of 64 sampling points, with the crystal faces approximated by 10 rational boundary planes. Values for the calculated transmission coefficients range from 0.830 to 0.968.²⁵ In all, 1993 reflections were collected which averaged to 1810 unique reflections for space group $P2_1/c$. Of these, 1210 reflections had intensities greater than 3σ .

Throughout data collection and in the subsequent structure analysis, the unit cell parameters used (Table I) were those from the earlier X-ray study.²¹ It is interesting to note that the reflections with odd l indices, which are exceedingly weak in the X-ray data set, are in general substantially stronger in the neutron data set.

Structure Analysis. At the outset of this structure analysis we felt it desirable to get independent proof that the solution of Owston et

**Figure 1.** Molecular geometry of the $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ anion.**Table II.** Final Positional Parameters for $\text{KPtCl}_3(\text{C}_2\text{H}_4)\cdot\text{H}_2\text{O}$

Atom	x	y	z
Pt	0.2862 (1)	0.2505 (2)	0.0595 (1)
Cl(1)	0.0763 (1)	0.2374 (2)	0.0537 (2)
Cl(2)	0.2848 (2)	0.5209 (2)	0.0926 (2)
Cl(3)	0.2917 (2)	0.9788 (2)	0.0364 (2)
C(1)	0.4390 (2)	0.2715 (4)	0.9734 (3)
C(2)	0.4856 (2)	0.2566 (4)	0.1212 (3)
H(1)	0.4304 (6)	0.3874 (8)	0.9199 (6)
H(2)	0.4358 (6)	0.1698 (8)	0.9034 (6)
H(3)	0.5173 (5)	0.3588 (8)	0.1896 (7)
H(4)	0.5224 (5)	0.1440 (9)	0.1704 (7)
K	0.9394 (4)	0.0452 (5)	0.2525 (5)
O	0.8528 (4)	0.3537 (4)	0.2309 (5)
H(5)	0.7945 (6)	0.3819 (8)	0.1372 (9)
H(6)	0.8124 (6)	0.3889 (8)	0.2973 (8)

al²¹ was in fact the correct one. This was done by applying direct methods²⁶ to the neutron diffraction data. The E map calculated from the phase set with the highest combined figure of merit confirmed all the atomic positions found in the X-ray study. These coordinates were used to generate a difference scattering density map, which revealed the positions of all hydrogen atoms.

The structure was refined isotropically by full-matrix least squares to an agreement factor R of 0.280 based on F^2 . It was observed that the most intense reflections showed F_c^2 greater than F_o^2 which indicated the presence of extinction. Refinement of an isotropic extinction parameter (g)²⁷ did not lead to convergence until all coordinate positions had been refined anisotropically and a damping factor of 0.5 applied to the shift for extinction. One reflection (040) was found to dominate the extinction refinement and so its influence was minimized by assigning to it a very small weight. The final value of $g (= 1.1 (1) \times 10^4)$ corresponds to a nominal mosaic spread of 5 sec.

Final agreement factors²⁸ based on F are as follows: for reflections with $F_o^2 > 0$, $R_F = 0.092$ and $R_{wF} = 0.081$; for data with $I > 3\sigma$, $R_F = 0.070$ and $R_{wF} = 0.076$. Agreement factors based on F^2 are as follows: for all reflections, $R_{F^2} = 0.120$ and $R_{wF^2} = 0.134$. All refinements were performed on F^2 , including reflections with $F_o^2 < 0$, as has been suggested by several authors.²⁹ The function minimized is $\sum w(F_o^2 - |F_c|^2)^2$, where $w = [\sigma_{\text{count}}^2(F_o^2) + (0.02F_o^2)^2]^{-1}$. Neutron scattering lengths were taken to be $b_{\text{Pt}} = 0.95$, $b_{\text{Cl}} = 0.9584$, $b_{\text{C}} = 0.37$, $b_{\text{O}} = 0.575$, $b_{\text{K}} = 0.6626$, and $b_{\text{H}} = -0.3723$ (in units of 10^{-12} cm).³⁰ A listing of observed and calculated structure factors is available.³¹

Description of the Structure

A diagram of the $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ anion is given in Figure 1. Final positional and thermal parameters are listed in Tables II and III, and bond lengths and angles in Tables IV and V, respectively.

As expected, the nonhydrogen portion of the structure agrees quite well with the results of the earlier X-ray study.²¹ The PtCl_3 moiety forms a nearly planar group with the platinum atom 0.03 \AA from the best plane through the PtCl_3 group. The ethylenic C-C bond forms an angle of 5.9° with the normal

Table III. Final Anisotropic Temperature Factors^a for $\text{KPtCl}_3(\text{C}_2\text{H}_4)\cdot\text{H}_2\text{O}$

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Pt	66 (1)	106 (2)	96 (2)	3 (1)	41 (1)	3 (2)
Cl(1)	71 (1)	141 (3)	193 (3)	-4 (2)	58 (2)	-2 (2)
Cl(2)	107 (2)	112 (2)	179 (3)	-7 (2)	63 (2)	-4 (2)
Cl(3)	116 (2)	112 (2)	190 (3)	13 (2)	71 (2)	-7 (2)
C(1)	109 (2)	188 (5)	149 (4)	-4 (3)	88 (3)	5 (4)
C(2)	74 (2)	207 (6)	161 (4)	0 (3)	53 (2)	5 (4)
H(1)	177 (7)	255 (12)	213 (10)	-16 (8)	116 (7)	56 (9)
H(2)	188 (8)	266 (12)	183 (9)	37 (8)	118 (7)	-14 (8)
H(3)	109 (6)	273 (13)	206 (9)	-46 (7)	41 (6)	-42 (9)
H(4)	106 (6)	294 (14)	251 (11)	54 (7)	46 (6)	59 (10)
K	110 (5)	138 (7)	188 (7)	-3 (4)	64 (5)	19 (6)
O	121 (4)	170 (6)	159 (6)	21 (4)	56 (4)	1 (5)
H(5)	139 (7)	259 (13)	232 (11)	31 (8)	52 (7)	-3 (11)
H(6)	185 (9)	277 (13)	233 (11)	36 (8)	113 (8)	-6 (10)

^a For the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Bond Distances in $\text{KPtCl}_3(\text{C}_2\text{H}_4)\cdot\text{H}_2\text{O}$

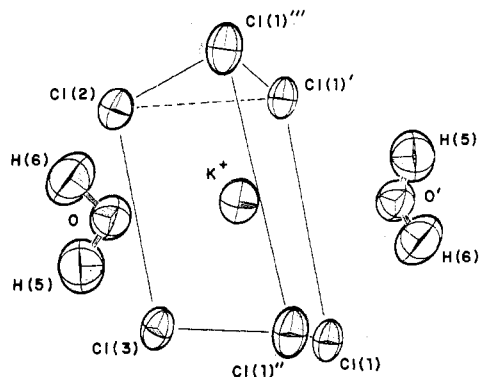
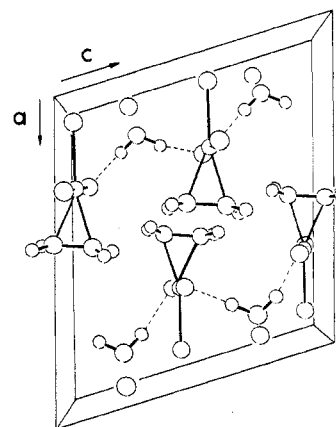
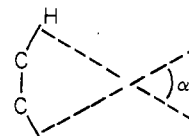
Atoms	Distance, Å	Atoms	Distance, Å
(a) Distances from the Platinum Atom			
Pt-Cl(1) (trans)	2.340 (2)		
Pt-Cl(2) (cis)	2.302 (2)	Pt-Cl(3) (cis)	2.303 (2)
Pt-C(1)	2.128 (3)	Pt-C(2)	2.135 (3)
(b) Distances within the Ethylene Group			
C(1)-C(2)	1.375 (4)		
C(1)-H(1)	1.096 (7)	C(1)-H(2)	1.087 (7)
C(2)-H(3)	1.079 (8)	C(2)-H(4)	1.086 (8)
(c) Distances within the Hydrogen-Bonding Network			
O-H(5)	0.975 (9)	O-H(6)	0.940 (8)
H(5)···Cl(2)	2.288 (8)	H(6)···Cl(3)	2.380 (8)
O···Cl(2)	3.228 (5)	O···Cl(3)	3.320 (5)
(d) Distances around the Potassium Cation (See Figure 2)			
K···Cl(1)	3.768 (5)	K···Cl(1)'	3.237 (5)
K···Cl(1)''	3.236 (5)	K···Cl(1)'''	3.397 (5)
K···Cl(2)	3.299 (5)	K···Cl(3)	3.199 (5)
K···O	2.761 (6)	K···O'	2.798 (6)

Table V. Bond Angles in $\text{KPtCl}_3(\text{C}_2\text{H}_4)\cdot\text{H}_2\text{O}$

Atoms	Angle, deg	Atoms	Angle, deg
(a) Angles around the Platinum Atom			
Cl(1)-Pt-Cl(2)	90.05 (8)	Cl(1)-Pt-Cl(3)	90.43 (8)
Cl(2)-Pt-Cl(3)	177.65 (9)	C(1)-Pt-C(2)	37.6 (1)
(b) Angles within the Ethylene Group			
Pt-C(1)-C(2)	71.4 (2)	Pt-C(2)-C(1)	70.9 (2)
H(1)-C(1)-H(2)	115.2 (5)	H(1)-C(1)-C(2)	121.7 (4)
H(2)-C(1)-C(2)	120.6 (4)	H(3)-C(2)-H(4)	114.6 (6)
H(3)-C(2)-C(1)	121.2 (5)	H(4)-C(2)-C(1)	120.8 (5)
(c) Angles within the Hydrogen Bonding System			
H(5)-O-H(6)	103.6 (6)		
O-H(5)···Cl(2)	161.6 (7)	O-H(6)···Cl(3)	179.4 (7)
Pt-Cl(2)···H(5)	103.6 (2)	Pt-Cl(3)···H(6)	102.5 (2)

to this plane, and the central point between the two carbon atoms is 0.22 Å from the PtCl_3 plane. The two ethylenic carbon atoms are equidistant from the platinum atom within the limits of experimental accuracy [$\text{Pt}-\text{C}(1) = 2.128 (3) \text{ \AA}$; $\text{Pt}-\text{C}(2) = 2.135 (3) \text{ \AA}$] and are separated by 1.375 (4) Å. The distance from the midpoint of the C-C bond to the Pt atom is 2.022 (3) Å.

The Pt-Cl bond trans to the ethylene [2.340 (2) Å] is longer than the average of the two cis Pt-Cl bonds [2.302 (2) Å], with a difference (0.038 Å) corresponding to 19 standard deviations. The hydrogen atoms of the ethylene group are symmetrically bent away from the central platinum atom and form an angle, α , of 32.5°, where α is defined³² as the angle between the normals to the H-C-H planes, i.e.

**Figure 2.** Coordination about the K^+ ion.**Figure 3.** Projection of the unit cell of Zeise's salt down the b axis, showing a portion of the hydrogen-bonding framework involving the hydrogen atoms of the water molecules.

The distances of carbon atoms C(1) and C(2) from the least-squares plane defined by the four hydrogen atoms are 0.158 and 0.171 Å, respectively, and the platinum atom is 2.185 Å from this plane.

The chloride ligands of the $\text{PtCl}_3(\text{C}_2\text{H}_4)$ anion form a distorted trigonal prism around the potassium cation (Figure 2). The two cis chlorines [Cl(2), Cl(3)] each have one near approach to K^+ , whereas the one trans chlorine has four interactions with K^+ ions. The water of hydration caps two rectangular faces of the trigonal prism and possesses an approximate tetrahedral coordination with two equivalent K^+ ions and two hydrogen bonds to nonequivalent Cl atoms. The resulting network of hydrogen bonds, composed of the series $-\text{Pt}-\text{cis Cl}\cdots\text{H}-\text{O}-\text{H}\cdots\text{cis Cl}-\text{Pt}-$, forms an infinite chain parallel to the bc plane (Figure 3).

Discussion

Trans Effect of Ethylene. Since ethylene is one of the strongest trans-activating ligands known, it was of interest to see if its presence would cause detectable distortions in the PtCl_3 fragment. Bond lengthening of the trans Pt-Cl bond relative to the cis Pt-Cl bonds was observed in the X-ray study of Zeise's salt by Owston et al.,²¹ but the differences they observed, which were of the order of two standard deviations (2σ), were considered too small to be conclusively meaningful. In the present neutron diffraction work, however, the cis and trans bond lengths differ by about 19σ , while the two cis Pt-Cl bonds agree within 1σ (Table IV). Thus the lengthening of the trans Pt-Cl bond in Zeise's salt is, for the first time, shown

Table VI. Comparison between Ethylene and TCNE Complexes

Compd	C-C, Å	$\Delta(\text{C-C})$, ^a Å	α , ^b deg	Method	Ref
C ₂ H ₄	1.337 (2)	0.0	0.0	c	22
Rh(C ₂ H ₄)(C ₂ F ₄)(C ₂ H ₅)	1.358 (9)	0.021	42.4	d	34
KPt(C ₂ H ₄)Cl ₃ ·H ₂ O	1.375 (4)	0.038	32.5	e	This work
Nb(C ₂ H ₄)(C ₂ H ₅)(C ₂ H ₅) ₂	1.406 (13)	0.069	52.5	d	36
C ₂ (CN) ₄	1.344 (3)	0.0	0.0	d	37
Ni[C ₂ (CN) ₄](t-C ₄ H ₉ NC) ₂	1.476 (5)	0.132	56.8	d	32
Ir[C ₂ (CN) ₄](CO)(Br)(PPh ₃) ₂	1.506 (15)	0.162	70.4	d	38
Ir[C ₂ (CN) ₄](CO)(C ₆ N ₄ H)(PPh ₃) ₂	1.526 (12)	0.182	67.4	d	33

^a $\Delta(\text{C-C})$ is the difference between the C-C distances of the complexed and uncomplexed forms of the ligand. ^b α is the angle between the normals to the two CH₂ or C(CN)₂ planes (see ref 32). ^c Electron diffraction. ^d X-Ray diffraction. ^e Neutron diffraction.

to be significant. The added precision of the neutron diffraction method is largely due to (i) the fact that the platinum atom does not dominate the scattering process the way it does in X-ray diffraction and (ii) the lack of scattering angle dependence of neutron scattering factors. These differences allow the light atom positions to be determined with high precision.

The individual Pt-Cl distances may also be affected by the pattern of K⁺...Cl interactions in the unit cell. The trans chlorine atom is in a unique position within a potassium cavity (having four interactions with the potassium cation vs. one interaction for the cis-chlorine atoms). Thus, even though it is reasonable to assume that the major cause of the lengthening of the trans Pt-Cl bond is the trans effect of the ethylene ligand, the magnitude of distortion may be significantly affected by the K⁺...Cl interactions described here.

Geometry of the Ethylene Ligand. According to the Dewar-Chatto-Duncanson model for olefin bonding,^{7,8} electron density from a 5d_{6p} hybrid orbital is donated into the π^* antibonding orbital of ethylene. One would expect to see from this process noticeable distortions of the ethylene ligand from the planarity imposed by sp² hybridization and noticeable lengthening of the olefin carbon-carbon double bond.

The C-C bond length in Zeise's salt [1.375 (4) Å] agrees well with the X-ray measurement of Owston et al. [1.37 (2) Å]²¹ and is slightly longer than the earlier neutron diffraction measurement in the wrong space group [1.354 (15) Å].²⁰ This distance is only 0.038 Å longer than that in free ethylene [1.337 (2) Å],²² in marked contrast to complexes of other substituted olefins, such as tetracyanoethylene (TCNE), in which increases in the range 0.13-0.19 Å are commonly found.³² Trends in C-C bond lengths and bending parameters (α angles) in olefin complexes have been thoroughly discussed by Ibers^{32,33} and Guggenberger.³⁴⁻³⁶ It is becoming clear that ethylene and other simple alkenes do not seem to show as much distortion in the complexed form as olefins with electronegative or delocalizable substituents such as C₂F₄ and C₂(CN)₄, which can function as better π acceptors. This is consistent with the observation that electron-withdrawing substituents on the olefin tend to increase the stability of the olefin complex.³⁹ Table VI, which compares several ethylene and TCNE complexes, shows that both bending (α) and bond-lengthening effects (Δ) are consistently smaller in ethylene than in TCNE complexes. One can reasonably conclude from these results that metal-ligand back-bonding in ethylene complexes, while present, is probably less pronounced than it is in C₂F₄ and C₂(CN)₄ complexes.

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Registry No. KPtCl₃(C₂H₄)·H₂O, 16405-35-9.

Supplementary Material Available. A listing of structure factor amplitudes 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

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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

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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 $a = 7.871(5) \text{ \AA}, b = 15.222(11) \text{ \AA}, c = 6.406(3) \text{ \AA},$ and $\beta = 95.58(3)^\circ$. Intensity data were collected with a four-circle computer-controlled diffractometer using the $\theta-2\theta$ 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) $\text{ \AA};$ C-S, 1.688 (4), 1.695 (4) $\text{ \AA};$ S-S(bite), 3.257 (2) $\text{ \AA};$ S-Ni-S(intraligand), 94.19 (6) $^\circ;$ S-S(interligand), 3.027 (2) $\text{ \AA};$ S-Ni-S(interligand) 85.81 (5) $^\circ$.

Introduction

The stereochemistry of monomeric bis(chelate)metal(II) dithiolene⁴ and 1,1-dithio⁵ 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 \AA). 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 \AA .

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 chromophore⁸ ($M = Co(II), Fe(II), Mn(II)$). Similarly with the structurally related diethyldithiophosphinate ligand $(S_2PEt_2^-)$, tetrahedral Co-S₄ and Zn-S₄ units have been found in dimeric complexes.⁹

Recently, Davison and Switkes¹⁰ 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 \AA in the iron(II) complex to 3.49 \AA 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 \AA . 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 dianion¹⁹ and its