

than the corresponding distance (3.147 (4) Å) in the amine analogue and may reflect this preference.

Observed Cu–S bond distances for the title complex (2.308 (2), 2.369 (2) Å) fall within the range of 2.30–2.45 Å reported by other workers for equatorial ligation of this type.^{8–11} In the square-pyramidal model with both S(1) and S(2) equatorial, the nonequivalence of these distances would be associated with the distorted nature of the CuS₂Cl₃ unit. With a trigonal-bipyramidal model having S(2) axial and S(1) equatorial, this nonequivalence could result from minimization of electron-pair repulsion which is expected¹⁹ to lead to a contraction of the axial bond relative to the equatorial bond for d⁹ complexes. Thus, the “axial” Cu–S(2) bond is shorter than the corresponding “equatorial” bond, in analogy with a trigonal-bipyramidal CuCl₅²⁻ complex²⁰ which revealed axial Cu–Cl bonds (2.296 (1) Å) approximately 0.1 Å shorter than the equatorial bonds (2.391 (1) Å). However, the trigonal-bipyramidal model would then be inconsistent with the observation that the Cu–Cl(1) bond (axial) is ~0.02 Å longer than the Cu–Cl(2) bond (equatorial).

With use of either model, the bridged Cu–Cu'–Cl(1)–Cl(1') fragment contains two equatorial Cu–Cl spans (2.266 (2) Å) and two apical Cu–Cl spans (2.825 (2) Å). Both Cu–Cl–Cu' bridging angles (94.22 (5)°) are required crystallographically to be equal. These structural features yield a Cu...Cu' separation of 3.749 (2) Å. Comparable parameters reported for the [(Me₂NCH₂CH₂NMe₂)CuCl₂]₂ complex include Cu–Cl spans of 2.264 (3) and 3.147 (4) Å, Cu–Cl–Cu bridging angles of 96.8 (1)°, and a Cu...Cu' separation of 4.089 (4) Å.⁷

Structural features of the ligand include uneventful C–C and C–S bond distances which, except in the vicinity of the disorder (C(2), vide supra), fall within the ranges reported by other workers for thioether ligands.^{8–11}

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Registry No. [Cu(BuSCH₂CH₂SBu)Cl₂]₂, 61128-82-3.

Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Neutral Complexes of Gallium(II) Containing Gallium–Gallium Bonds

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The complexes formed between the “gallium dihalides” (Ga₂X₄) and 1,4-dioxane (diox), Ga₂X₄·2(diox) (X = Cl, Br, I), have been reinvestigated. Ga₂Cl₄·2C₄H₈O₂ forms triclinic crystals, space group *P* $\bar{1}$, with *a* = 8.829 (5) Å, *b* = 9.101 (5) Å, *c* = 10.82 (1) Å, α = 107.27°, β = 97.73 (2)°, γ = 72.34 (2)°, *Z* = 2, *D*_{calc} = 1.943 g cm⁻³, and *D*_{meas} = 1.95 g cm⁻³. The structure has been solved from 3034 diffractometer-measured intensities with Mo K α radiation (λ 0.7107 Å) and refined by full-matrix least squares to *R* = 0.085. The crystal structure shows that the complex is a discrete molecule containing a gallium–gallium bond of length 2.406 (1) Å with dioxane acting as a monodentate ligand. Spectroscopic and other evidence is presented which shows that the bromide and iodide complexes have a similar structure.

Introduction

The “gallium dihalides” form many complexes with both monodentate and bidentate ligands. With monodentate ligands, these have the stoichiometry Ga₂X₄·4L, e.g., L = anisole and dimethyl sulfide, while with bidentate ligands they have stoichiometry Ga₂X₄·2L, e.g., L = 1,4-dioxane and morpholine.^{1–3} It has been proposed¹ that the complexes have

ionic formulations, e.g., Ga(C₆H₅OCH₃)₄⁺GaX₄⁻ and Ga(C₄H₈O₂)₂⁺GaX₄⁻ in which the metal is four-coordinate.

Evidence for such species comes mainly from electrical conductivity measurements of the complexes in nitrobenzene solution.¹ For the ion Ga(diox)₂⁺, evidence also comes from a crystal structure determination of the complex Ga(diox)₂Cl which may also be isolated from the reaction between Ga₂Cl₄

Table I

space group $P\bar{1}$	$\beta = 97.73 (2)^\circ$
$a = 8.829 (5) \text{ \AA}$	$\gamma = 72.34 (2)^\circ$
$b = 9.101 (5) \text{ \AA}$	$D_{\text{measd}} = 1.95 \text{ g cm}^{-3}$
$c = 10.82 (1) \text{ \AA}$	$D_{\text{calcd}} = 1.943 \text{ g cm}^{-3}$
$\alpha = 107.27 (2)^\circ$	$Z = 2$

and dioxane.² This crystal structure, however, is of low accuracy,⁴ being based upon limited crystal data, and is incompletely resolved. We were interested in preparing a series of complexes analogous to those formed by the boron halides $B_2X_4 \cdot 2L$. Since charged complexes of this type are known for gallium(II), e.g., $Ga_2X_6^{2-}$,⁵ it seemed reasonable that a series of neutral complexes should exist.

In the first instance, we have chosen to reexamine some of the compounds first prepared by Brewer et al.¹⁻³ and here we describe the dioxane complexes which have stoichiometries analogous to the boron series.

Experimental Section

The complexes are very susceptible to moisture and were prepared in an all-glass apparatus in vacuo, and subsequent manipulations were carried out in a nitrogen-filled drybox.

The complexes were prepared by two methods.

(1) The original method, using benzene solutions of halide and ligand, as described by Brewer¹ was used. Although products were obtained by this method, the one described below was found to be the most satisfactory.

(2) Excess dry dioxane was condensed onto pure Ga_2X_4 in vacuo. After the product was allowed to stand for several hours at 0 °C, the excess ligand was removed and white powder remained. These had stoichiometry $Ga_2X_4(\text{diox})_2$ (see Table V for analytical data).

Satisfactory crystals of the chloride complex were prepared by allowing a saturated dioxane solution of the complex to stand for several days when small crystals were deposited. The density of selected crystals was determined by flotation in a 1,2-dibromoethane/benzene mixture. The gallium dihalides were prepared by standard methods¹⁰ and dioxane was refluxed with sodium/potassium alloy for 24 h before being fractionally distilled.

Raman spectra were recorded on solid samples using a Cary 81 spectrometer.

X-ray Measurements. All measurements were made with a single crystal sealed in a Lindemann glass tube. The crystal data listed in Table I were obtained from Weissenberg photographs with $Cu K\alpha$ radiation ($\lambda 1.542 \text{ \AA}$). Intensity measurements were made on the Stoe STADI 2 two-circle automatic diffractometer with graphite-monochromatized $Mo K\alpha$ radiation ($\lambda 0.7107 \text{ \AA}$). Reciprocal lattice layers ($h = 0-10$) with the crystal set about the a axis were cross scaled with data from the zero layer with the crystal reset about the b axis. The crystal size was $0.6 \times 0.6 \times 0.5 \text{ mm}$, absorption corrections and scaling of data were carried out with the SHELX suite of programs.⁶ After elimination of those for which $I < 3\sigma(I)$, there remained 3034 unique reflections. The same programs were used for all other calculations. Gallium and chlorine atom positions were obtained from

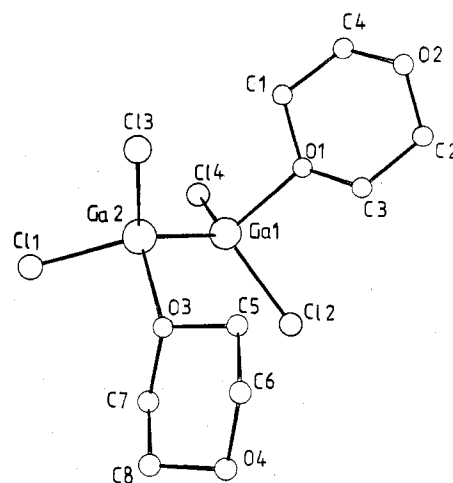


Figure 1.

Patterson maps. F_o Fourier maps phased on these atoms gave the positions of the remainder of the atoms (apart from the hydrogens). Full-matrix least-squares refinement of all atomic positions and anisotropic U_{ij} values were carried out until convergence was reached at $R = 0.085$, and in the later stages it was found that inclusion (without refinement) of the hydrogen atoms at their calculated positions gave improved agreement. A list of position and U_{ij} parameters is given in Table II, and a list of F_o and F_c is available as supplementary material. The atomic scattering factors used were those of Cromer and Mann.⁷

Results and Discussion

Raman spectra were recorded on solid samples and the observed frequencies between 100 and 500 cm^{-1} are tabulated (see Table IV).

The similarity in the positions of the very strong band in the spectra of the chloride and bromide complexes to those observed in $Ga_2Cl_6^{2-}$ (233 cm^{-1}) and $Ga_2Br_6^{2-}$ (164 cm^{-1}), which are known to have ethane-like structures with metal-metal bonds, suggested that these compounds might have similar structures and this view has been confirmed for the chloride by a single-crystal structure determination (described below).

Structure of $Ga_2Cl_4 \cdot 2(\text{diox})$

The formula unit is found to exist as a single discrete molecule, as shown in Figure 1; bond distances and angles are listed in Table III. The disposition of bonds around both gallium atoms is similar, being distorted tetrahedral. The data in Table III show that the Ga-Ga-O angles are tetrahedral as are the Cl-Ga-Cl angles, but the Ga-Ga-Cl angles are all appreciably greater than tetrahedral. The torsion angles about Ga(1)-Ga(2) shown in Figure 2 show that the molecule has

Table II. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Vibration Parameters ($U_{ij} \times 10^4$) with Standard Deviations in Parentheses

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga(1)	2757 (1)	1734 (1)	2511 (1)	467 (4)	591 (5)	401 (4)	74 (3)	12 (3)	-331 (3)
Ga(2)	2687 (1)	-728 (1)	904 (1)	460 (4)	556 (5)	410 (4)	85 (3)	-9 (3)	-280 (3)
Cl(1)	3464 (2)	-1194 (2)	-1027 (1)	624 (9)	799 (10)	414 (7)	134 (7)	-14 (7)	-343 (8)
Cl(2)	4820 (2)	1720 (3)	3867 (2)	513 (9)	1222 (16)	493 (8)	171 (9)	-35 (7)	-526 (10)
Cl(3)	732 (2)	-1769 (2)	796 (2)	527 (9)	746 (10)	852 (12)	190 (9)	1 (8)	-398 (8)
Cl(4)	1949 (2)	3963 (2)	1968 (2)	760 (12)	631 (9)	715 (11)	175 (8)	138 (9)	-339 (9)
O(1)	1137 (5)	2225 (6)	3836 (4)	377 (20)	727 (25)	447 (20)	176 (18)	-10 (16)	-319 (19)
O(2)	-1236 (6)	2340 (6)	5403 (5)	555 (2)	824 (32)	638 (27)	213 (23)	73 (22)	-386 (24)
O(3)	4436 (5)	-2506 (6)	1436 (4)	426 (22)	714 (25)	474 (22)	201 (19)	-12 (18)	-249 (20)
O(4)	6964 (7)	-4450 (7)	2591 (6)	572 (29)	884 (35)	825 (36)	359 (29)	-115 (27)	-288 (27)
C(1)	-510 (7)	2357 (10)	3331 (7)	382 (30)	887 (46)	596 (36)	240 (34)	-70 (27)	-303 (31)
C(2)	358 (9)	2232 (10)	5879 (7)	629 (41)	974 (53)	564 (36)	313 (36)	21 (31)	-433 (39)
C(3)	1502 (8)	1359 (10)	4845 (7)	439 (31)	917 (48)	593 (36)	362 (35)	-15 (27)	-346 (32)
C(4)	-1600 (9)	3181 (10)	4425 (8)	472 (35)	798 (46)	739 (45)	227 (37)	62 (33)	-263 (33)
C(5)	4256 (10)	-2788 (9)	2651 (7)	714 (44)	721 (40)	529 (34)	194 (30)	85 (32)	-307 (35)
C(6)	5364 (10)	-4363 (10)	2727 (9)	670 (47)	764 (46)	931 (56)	457 (44)	-126 (42)	-300 (39)
C(7)	6102 (8)	-2606 (10)	1283 (7)	423 (33)	945 (51)	651 (39)	286 (36)	-18 (29)	-349 (34)
C(8)	7113 (9)	-4200 (10)	1376 (8)	513 (36)	856 (48)	690 (42)	257 (38)	19 (34)	-170 (35)

Table III. Bond Distances (Å) and Angles (deg) and Their Standard Deviations

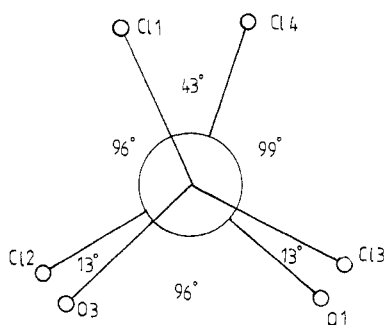
Distances			
Ga(1)-Ga(2)	2.406 (1)	O(2)-C(2)	1.417 (9)
Ga(1)-Cl(2)	2.179 (2)	C(2)-C(3)	1.481 (10)
Ga(1)-Cl(4)	2.165 (2)	C(3)-O(1)	1.476 (11)
Ga(1)-O(1)	2.021 (5)	O(3)-C(5)	1.449 (10)
Ga(2)-Cl(1)	2.168 (2)	C(5)-C(6)	1.490 (10)
Ga(2)-Cl(3)	2.182 (2)	C(6)-O(4)	1.416 (11)
Ga(2)-O(3)	2.033 (5)	O(4)-C(8)	1.428 (12)
O(1)-C(1)	1.465 (7)	C(8)-C(7)	1.485 (11)
C(1)-C(4)	1.494 (10)	C(7)-O(3)	1.480 (9)
C(4)-O(2)	1.432 (11)		

Angles			
Ga(2)-Ga(1)-Cl(2)	118.05 (7)	Ga(2)-O(3)-C(5)	116.2 (4)
Ga(2)-Ga(1)-Cl(4)	119.29 (7)	Ga(2)-O(3)-C(7)	117.7 (5)
Ga(2)-Ga(1)-O(1)	108.96 (15)	C(3)-O(1)-C(1)	109.7 (6)
Cl(2)-Ga(1)-Cl(4)	110.66 (10)	O(1)-C(1)-C(4)	109.1 (5)
Cl(2)-Ga(1)-O(1)	96.69 (14)	C(1)-C(4)-O(2)	111.5 (6)
Cl(4)-Ga(1)-O(1)	98.59 (16)	C(4)-O(2)-C(2)	109.0 (7)
Ga(1)-Ga(2)-Cl(1)	120.11 (8)	O(2)-C(2)-C(3)	112.0 (6)
Ga(1)-Ga(2)-Cl(3)	120.34 (6)	C(2)-C(3)-O(1)	108.5 (6)
Ga(1)-Ga(2)-O(3)	106.92 (13)	C(5)-O(3)-C(7)	112.2 (5)
Cl(1)-Ga(2)-Cl(3)	109.64 (8)	O(3)-C(7)-C(8)	107.8 (8)
Cl(1)-Ga(2)-O(3)	97.08 (14)	C(7)-C(8)-O(4)	111.8 (6)
Cl(3)-Ga(2)-O(3)	96.89 (17)	C(8)-O(4)-C(6)	109.9 (6)
Ga(1)-O(1)-C(1)	116.0 (4)	O(4)-C(6)-C(5)	111.9 (8)
Ga(1)-O(1)-C(3)	119.7 (3)	C(6)-C(5)-O(3)	109.2 (6)

Table IV. Torsion Angles (deg) and Least-Squares Planes

Torsion Angles			
Ga(1)-Ga(2)-O(3)-C(5)	63.8	Ga(1)-Ga(2)-O(3)-C(7)	-72.5
Ga(2)-Ga(1)-O(1)-C(1)	-57.4	Ga(2)-Ga(1)-O(1)-C(3)	77.8

Least-Squares Planes					
plane defined by	atom	dist from plane, Å	plane defined by	atom	dist from plane, Å
O(1), C(1), C(4), O(2)	O(1)	0.242	O(3), C(5), C(6), O(4)	O(3)	-0.232
C(2), C(3)	C(1)	-0.235	C(8), C(7)	C(5)	0.220
	C(4)	0.229		C(6)	-0.233
	O(2)	-0.236		O(4)	0.239
	C(2)	0.240		C(8)	-0.242
	C(3)	-0.240		C(7)	0.238
	Ga(1)	0.196		Ga(2)	-0.164

**Figure 2.**

an almost eclipsed conformation with the oxygen atoms opposed to chlorines. The torsion angle values about the Ga-O bonds and least-squares planes through the dioxane rings given in Table IV show that O-Ga ligands lie somewhere between the equatorial tetrahedral and the planar conformation with respect to the C-O-C bonds. The data in Table IV show that although the twists of the dioxane rings relative to the Ga-Ga bond are similar, they are not identical. The closest intermolecular contacts of O(2) and O(4) are to hydrogen atoms, 2.38 and 2.70 Å, respectively (the corresponding carbon atoms are 3.37 and 3.50 Å distant).

The Ga-Ga distance 2.406 (1) Å compares favorably with that found in the $\text{Ga}_2\text{Cl}_6^{2-}$ ion (2.390 (2) Å). However, a major difference between the structures occurs in that the ion

Table V. Analytical Data for Dioxane Complexes

compd	found		calcd	
	% Ga	% X	% Ga	% X
$\text{Ga}_2\text{Cl}_4 \cdot 2(\text{diox})$	30.21	30.70	30.50	31.00
$\text{Ga}_2\text{Br}_4 \cdot 2(\text{diox})$	21.80	50.44	22.00	50.30
$\text{Ga}_2\text{I}_4 \cdot 2(\text{diox})$	16.70	60.90	16.94	61.66

Table VI. Raman Spectra of $\text{Ga}_2\text{X}_4 \cdot 2(\text{diox})$ (cm^{-1})

$\text{Ga}_2\text{Cl}_4 \cdot 2(\text{diox})$	$\text{Ga}_2\text{Br}_4 \cdot 2(\text{diox})$	$\text{Ga}_2\text{I}_4 \cdot 2(\text{diox})$
483 m	485 w	485 w
465 w	327 m	306 w
396 m	286 m	242 w
375 m	274 m	230 w
340 w	242 m	143 vvs
238 vvs	210 m	
113 s	196 m	
	169 vvs	

Table VII. Raman Spectra of $\text{Ga}_2\text{X}_6^{2-}$ Ions (cm^{-1})⁵

$\text{Ga}_2\text{Cl}_6^{2-}$	$\text{Ga}_2\text{Br}_6^{2-}$	$\text{Ga}_2\text{I}_6^{2-}$	assignt
ν_2 233 vs	164 vvs	118 vvs	a_{1g} in-phase str
ν_4 314 w	228 m, 236 sh	184 m, 190 sh	e_g Ga-X str
ν_1 375 m	311 m	285 s	a_{1g} out-of-phase str

adopts the expected staggered structure⁸ while the neutral complex is essentially eclipsed.

In the eclipsed form, there will be more repulsion between the halogen atoms bonded to different galliums. This is reflected in the increased Ga-Ga-Cl angle of $\sim 119^\circ$ in the neutral complex and $113.9(1)^\circ$ in the anion.

Several additional features emerge from the crystal structures which merit discussion. The ligand dioxane is in the chair form and is monodentate. A boat form has been reported for the analogous $\text{Ga}(\text{diox})_2\text{Cl}_2$.² The monodentate nature of the ligand is surprising since there are numerous examples of bidentate dioxane complexes. This is attributed to the preference of gallium for four-coordination, since bidentate dioxane would lead to the less stable five-coordination.

The Raman spectra of $\text{Ga}_2\text{Cl}_4 \cdot 2(\text{diox})$ and $\text{Ga}_2\text{Br}_4 \cdot 2(\text{diox})$ have similarities with the anions $\text{Ga}_2\text{Br}_6^{2-}$ and $\text{Ga}_2\text{Cl}_6^{2-}$, and we propose that the bromide complex has a similar metal-metal bonded structure.

The anions have been discussed in detail by Taylor et al.⁵ In the anions $\text{Ga}_2\text{X}_6^{2-}$ (X = Cl, Br, I) there are three stretching modes which are Raman active. These are shown with assignments in Table VII.

Extensive mixing of the Ga-Ga and Ga-X stretching modes occur so that neither of the a_{1g} modes may be described as a localized Ga-Ga stretching or Ga-X stretching mode. The most intense band is assigned to a totally symmetrical mode in which all gallium-halogen bonds stretch in phase with the stretching of the gallium-gallium bond, and Taylor⁹ has shown that this intense band may be used in identification of compounds containing gallium-gallium bonds.

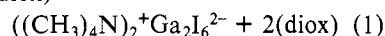
The spectra of the chloride and bromide dioxane complexes are more complex than those of the anions which is not surprising since they are noncentrosymmetric and additional modes will become Raman active. However, they both have the very intense bands characteristic of the gallium-gallium bonded complexes and these bands are close to those found in the halide ions.

Assignment of the less intense bands is very difficult in view of the mixing. No obvious band due to Ga-O stretching is observed in either compound (the bands at 483 cm^{-1} are discounted since they occur in pure dioxane) which suggests that extensive mixing of this mode is also occurring.

The Raman spectrum of $\text{Ga}_2\text{I}_4 \cdot 2(\text{diox})$ differs markedly from that found for $\text{Ga}_2\text{I}_6^{2-}$ with a very intense band at 143

cm⁻¹. The spectrum has some similarity with that of the GaI₄⁻ ion (143 (vs), 214 (w), 235 (w) cm⁻¹) and would therefore be formulated Ga(diox)₂⁺ GaI₄⁻ as was first proposed by Brewer et al.³ However, the presence of a higher weak band at 306 cm⁻¹ suggests that the structure may also be metal-metal bonded. There is strong chemical evidence to support this view.

First, the complex readily reacts with tetramethylammonium iodide as in eq 1, indicating that the gallium-gallium bond 2(CH₃)₄NI + Ga₂I₄·2(diox) →



is retained on substitution of the iodide ion. Second, the ligand-replacement reaction shown in eq 2 occurs with pyridine. If an ionic complex, as proposed by Brewer et al.,³ is



present, then it would be expected that four pyridine molecules would displace bidentate dioxane. In both reactions the products were confirmed by chemical analysis and Raman spectra. The shift in the frequency of the very strong band in Ga₂I₆²⁻ (118 cm⁻¹) to 143 cm⁻¹ in Ga₂I₄·2(diox) is not surprising in view of the work of Taylor⁹ on mixed-halide species Ga₂X_{6-r}Y_r²⁻ (r = 0-6). He found that in these species the frequency of the in-phase A₁ mode changes appreciably on halide-ion replacement and appears to be mainly associated with mass change. Thus, in Ga₂I₄Cl₂²⁻, the intense band occurs at 145 cm⁻¹.

In summary, this investigation shows conclusively that the Ga₂Cl₄·2(diox) complex is a discrete molecule containing a gallium-gallium bond and is the first example of a neutral complex of the unknown Cl₂-Ga-Ga-Cl₂. It also provides a rare example of dioxane behaving as a monodentate ligand toward a metal.

Spectroscopic and other evidence strongly suggest that the structure of analogous bromide and iodide complexes are similar.

Registry No. Ga₂Cl₄·2(diox), 68317-88-4; Ga₂Br₄·2(diox), 68317-89-5; Ga₂I₄·2(diox), 68317-90-8.

Supplementary Material Available: A listing of observed and calculated structure factors (18 pages). Ordering information is given on any current mast head page.

References and Notes

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Structures of (Sulfur dioxide)tris(triphenylphosphine)nickel(0), Ni(SO₂)(PPh₃)₃, and Bis(sulfur dioxide)bis(triphenylphosphine)nickel(0), Ni(SO₂)₂(PPh₃)₂¹

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The structures of Ni(SO₂)(PPh₃)₃ (I) and Ni(SO₂)₂(PPh₃)₂ (II) have been determined by three-dimensional X-ray diffraction techniques. Complex I crystallized in the space group *P2₁/n* with lattice constants of *a* = 11.39 (2) Å, *b* = 31.01 (3) Å, *c* = 13.11 (2) Å, and β = 95.34 (9)° and was refined to an unweighted *R* value of 0.080 for 3635 reflections for which *I* ≥ 2σ(*I*). Complex II crystallized in the space group *P2₁/c* with lattice constants of *a* = 19.427 (6) Å, *b* = 10.370 (6) Å, *c* = 17.702 (6) Å, β = 112.62 (2)°, and *Z* = 4 (Mo Kα₁ radiation, λ 0.7093 Å) and was refined to an unweighted *R* value of 0.078 for 1483 reflections for which *I* ≥ 3σ(*I*). The sulfur dioxide groups are S bonded in both complexes and are coplanar with their respective Ni-S bonds. For complex II, the two SO₂ groups are nearly coplanar with each other, the dihedral angle between them being 23.5°. The angles about the nickel atoms are nearly tetrahedral in both complexes with NiS distances of 2.06 (1) and 2.08 (1) Å for II and 2.038 (4) Å for I. Complex I exhibits an average S-O distance of 1.448 (5) Å and an O-S-O angle of 113.4 (4)° while the values for II are 1.39 (1) Å and 115.5 (1)°. The significance of these structures relative to the isoelectronic complexes Pt(SO₂)(PPh₃)₃ and Pt(SO₂)₂(PPh₃)₂, which exhibit pyramidal geometry at the sulfur atom, is discussed.

Introduction

The amphoteric nature of sulfur dioxide with respect to its interaction with transition-metal centers, although structurally illustrated several years ago,²⁻⁴ has recently been a subject of renewed interest. This is due, at least in part, to the recent suggestion⁵ that while the bonding principles which govern this behavior for sulfur dioxide are similar to those for nitrosyl complexes,⁴ the differences are sufficient to make a thorough study of SO₂ systems worthwhile. It was indicated, on the basis of extended Hückel calculations^{5,6} (see especially ref 6), that for the four-coordinate d¹⁰ transition-metal systems the M-SO₂ bonding should be more sensitive to the basicity of the transition-metal center (and, therefore, the nature of the ancillary ligands) than for other electronic configurations and coordination types.⁵ The structural evidence tends to support this view, and there now exist four complexes of this type, two

of which (Pt(SO₂)(PPh₃)₃)⁶ and Pt(SO₂)₂(PPh₃)₂)⁷ exhibit pyramidal geometry at the sulfur atoms and two of which (Ni(SO₂)p₃)⁸ [p₃ = 1,1,1-tris((diphenylphosphino)methyl)ethane] and Co(NO)(SO₂)(PPh₃)₂)⁹ contain coplanar M-SO₂ groups. A third possibility which was unexpected and as yet not fully understood, i.e., the η² type of bonding, in which the sulfur-metal and one of the oxygen-metal distances are nearly equal, was discovered in the Rh(NO)(SO₂)(PPh₃)₂)¹⁰ complex and has subsequently been shown to exist in the complexes RuCl(NO)(SO₂)(PPh₃)₂)¹¹ Mo(SO₂)(CO)₃(phen)¹² and Mo(SO₂)₂(CO)₂(bpy).¹²

The question as to whether the difference between the modes of bonding, when the SO₂ is bound solely through the sulfur atom, is due primarily to inherent differences in metal basicity is not answered by the available structural data. The p₃ ligand, for example, constrains the P-Ni-P angles to be somewhat