

radii,¹⁷ it is possibly significantly shorter than the values of 2.01 (3) and 1.98 (3) Å observed in the saturated heterocycles $S(C_2H_4)_2SeBr_2$ ¹⁹ and $O(C_2H_4)_2SeICl$ ²⁰ in which no π bonding exists. In addition, the 1.905 (10) Å value is not significantly longer than the average Se-C distance of 1.87 (1) Å in the $Ni(Se_2CN(C_2H_5)_2)_2$ complex¹⁸ or the corresponding value of 1.86 (1) Å found in the trigonal prismatic diselenolene complex $Mo(Se_2C_2(CF_3)_2)_3$ ²¹ in which some π delocalization over the chelate ring is presumed to exist. However, the

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fact that some Se-C multiple-bond character may exist in the present structure must not be interpreted to mean that any significant π bonding between the Ni and Se atoms occurs in this complex. Further structural studies seem necessary before definite conclusions concerning the bonding in selenium donor chelates can be unequivocally established.

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The Crystal and Molecular Structure of Isothiocyanatothiocyanato-(1-diphenylphosphino-3-dimethylaminopropane)palladium(II)

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The orange compound $Pd[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2](SCN)(NCS)$ is monoclinic, with cell parameters $a = 11.684 \pm 0.003$, $b = 12.961 \pm 0.004$, $c = 14.641 \pm 0.003$ Å, and $\beta = 110.04 \pm 0.01^\circ$. The space group is $P2_1/c$ with four molecules per unit cell, $d_c = 1.578 \pm 0.002$ g/cm³ and $d_m = 1.567 \pm 0.005$ g/cm³. Diffractometer data were collected for Cu K α radiation and the structure has been refined by least-squares methods with anisotropic thermal parameters to a final R of 0.041 for 2716 observed reflections. The palladium atom is four-coordinated in a square-planar arrangement. The donor atoms are the phosphorus and nitrogen atoms of the organic ligand and one nitrogen and one sulfur atom from each thiocyanate group. They are arranged with the isothiocyanate linkage trans to the phosphorus atom and the thiocyanate linkage trans to the amine nitrogen atom. Bond distances about the palladium atom show a shortening (Pd-P = 2.243 ± 0.002 Å; Pd-S = 2.295 ± 0.002 Å) and a lengthening (Pd-N(ligand) = 2.147 ± 0.006 Å; Pd-N(NCS) = 2.063 ± 0.007 Å) consistent with a trans effect.

Introduction

The subtle factors influencing the formation of inorganic linkage isomers and particularly those involving the thiocyanate group¹ are of recent interest. A few compounds have been prepared which are reported to contain both metal-NCS and metal-SCN bonds (non-bridging) in the same molecule.²⁻⁵ The evidence for these linkage isomers has been based entirely on physical measurements in solution. However, the interpretation of the spectral data has not been conclusive since the C-N or C-S stretching frequencies may be masked by broad bands from other ligands³ or they may coincide with intense overtones from the N-C-S deformation mode.⁶

Only three X-ray structural studies have been re-

ported on compounds postulated to have S- and N-bonded thiocyanate groups. The compound $Pd(4,7\text{-diphenylphen})(SCN)_2$ was amorphous.² One ionic and one nitrogen-bonded thiocyanate group was found in $[Cu(N(CH_2CH_2NH_2)_3)(NCS)(NCS)]^{7,8}$ and bridging -N-C-S- groups were found in bis(ethylenethiourea)-cadmium thiocyanate.⁹

The compound $Pd[(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2](SCN)(NCS)$ was also believed to exhibit mixed bonding in the solid state¹⁰ and we undertook an X-ray examination of this compound to provide structural evidence for this hypothesis. A preliminary report of our results has appeared recently.¹¹

Experimental Section

Orange, polyhedral crystals of the complex were kindly supplied by Professor D. W. Meek. Preliminary Weissenberg and precession photographs indicated that the crystals were mono-

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clinic. The systematic absences of $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group to be $P2_1/c$ (C_{2h}^b).

A crystal was cleaved to give a fragment $0.074 \times 0.079 \times 0.084$ mm which was mounted on a glass fiber. The crystal was aligned on a General Electric single-crystal orienter with the reciprocal lattice vector 502 parallel to the ϕ axis of the orienter. Unit cell dimensions were obtained by a least-squares fit of 19 2θ values measured for the Cu $K\beta$ (λ 1.39217 Å) peak with a takeoff angle of 1° . The final lattice constants are $a = 11.684 \pm 0.003$ Å, $b = 12.961 \pm 0.004$ Å, $c = 14.641 \pm 0.003$ Å, and $\beta = 110.04 \pm 0.01^\circ$. The density calculated for four molecules per unit cell is 1.578 ± 0.002 g/cm³; the density determined by flotation in a carbon tetrachloride-cyclohexane solution is 1.567 ± 0.005 g/cm³.

Intensity data were measured with a General Electric XRD-6 diffractometer using Cu $K\alpha$ (λ 1.54051 Å) radiation with a take-off angle of 4° . A 0.35-mil Ni foil was placed in front of the counter window. A 20-sec count was taken using the stationary-crystal, stationary-counter technique. Four standard reflections were measured after every 100 reflections to check crystal and instrument stability. A decrease of less than 5% was noted and six scale factors were introduced to compensate for the loss of intensity in the standard reflections. Initially a unique set of reflections was measured and then the entire hemisphere was remeasured giving up to three estimations of each unique reflection. A background curve as a function of 2θ was obtained by measuring the background at various points in the hemisphere and averaging the counts obtained at a given 2θ value. A reflection was considered to be observed if the total counts exceeded the sum of the background plus 3 times the square root of the background. After equivalent reflections were averaged, the 12,523 measurements were reduced to 2716 observed and 1043 unobserved reflections. The unobserved reflections were entered as half the minimum observable counts and were identified by a negative value for the intensity. An empirical correction (based on scanned data from previous crystals) for the $\alpha_1 - \alpha_2$ splitting was made and then these data were reduced to a set of observed amplitudes on an arbitrary scale by application of Lorentz-polarization corrections. The linear absorption coefficient (μ) for the crystal with Cu $K\alpha$ radiation is 99.4 cm⁻¹, with the value of μr varying from 0.37 to 0.68. This variation could produce a 30% error in the intensity in the extreme case; however, the variation of intensity as a function of ϕ (at $\chi = 90^\circ$) suggests that the average error was much less.

Solution and Refinement of the Structure

The positions of the palladium atom and the coordinated phosphorus and sulfur atoms were located in a three-dimensional sharpened Patterson function. The second sulfur atom was located in a minimum function based on the palladium-palladium vector. The light atoms were located in a Fourier synthesis based on phases calculated from the palladium, phosphorus, and two sulfur atoms. Two full-matrix least-squares cycles using isotropic thermal parameters reduced R , the usual residual, to 0.089. The weighting scheme used was

$$\begin{aligned}\sqrt{w} &= F_0/F(\text{low}) \text{ if } F_0 < F(\text{low}) \\ \sqrt{w} &= 1 \text{ if } F(\text{low}) \leq F_0 \leq F(\text{high}) \\ \sqrt{w} &= F(\text{high})/F_0 \text{ if } F_0 > F(\text{high})\end{aligned}$$

where $F(\text{low})$ was 20.0 and $F(\text{high})$ was 120.0 (approximately $2.5F_0(\text{minimum})$ and $15F_0(\text{minimum})$, respectively). The value of $F(\text{low})$ was raised to 25.0 since some of the weaker reflections appeared unreliable. Eight least-squares cycles using a 3×3 block for positional parameters and a 6×6 block for individual anisotropic thermal parameters reduced R to 4.1%. The

TABLE I
THE FINAL POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x/a	y/b	z/c
Pd	0.14931 (4)	0.18570 (4)	0.06147 (4)
S1	0.32272 (17)	0.09676 (18)	0.14727 (17)
S2	-0.10154 (20)	-0.04728 (18)	0.16607 (18)
P1	0.27068 (15)	0.28884 (13)	0.01188 (13)
N1	-0.0088 (5)	0.2773 (5)	-0.0116 (5)
N2	0.0403 (5)	0.0877 (5)	0.1068 (5)
N3	0.2718 (8)	-0.0470 (7)	0.2708 (6)
C1	0.2853 (7)	0.0133 (6)	0.2181 (6)
C2	-0.0180 (6)	0.0309 (5)	0.1307 (5)
C3	-0.0540 (8)	0.3159 (9)	0.0680 (7)
C4	-0.1070 (7)	0.2105 (7)	-0.0786 (7)
C5	0.0105 (9)	0.3717 (7)	-0.0636 (8)
C6	0.0622 (10)	0.3537 (10)	-0.1433 (7)
C7	0.1942 (7)	0.3201 (7)	-0.1166 (5)
C8	0.3087 (6)	0.4103 (5)	0.0773 (5)
C9	0.2960 (7)	0.4197 (6)	0.1687 (5)
C10	0.3297 (7)	0.5113 (6)	0.2199 (6)
C11	0.3774 (7)	0.5920 (6)	0.1828 (6)
C12	0.3903 (7)	0.5819 (6)	0.0914 (6)
C13	0.3550 (7)	0.4915 (6)	0.0390 (5)
C14	0.4173 (6)	0.2364 (5)	0.0183 (6)
C15	0.5236 (7)	0.2683 (6)	0.0919 (6)
C16	0.6364 (8)	0.2240 (7)	0.0982 (7)
C17	0.6382 (8)	0.1485 (7)	0.0301 (7)
C18	0.5330 (9)	0.1183 (8)	-0.0452 (9)
C19	0.4202 (8)	0.1612 (6)	-0.0491 (8)

TABLE II
FINAL THERMAL PARAMETERS ($\times 10^4$) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	43 (0)	35 (0)	44 (0)	4 (1)	31 (0)	8 (1)
S1	56 (2)	71 (2)	74 (1)	45 (3)	44 (3)	65 (3)
S2	95 (2)	68 (2)	81 (2)	-64 (3)	89 (3)	-1 (3)
P1	54 (1)	33 (1)	40 (1)	-4 (2)	42 (2)	4 (2)
N1	49 (5)	48 (4)	65 (4)	37 (7)	16 (7)	14 (7)
N2	69 (6)	59 (5)	64 (4)	-17 (8)	56 (8)	21 (7)
N3	144 (10)	100 (7)	81 (6)	47 (14)	63 (12)	77 (11)
C1	89 (8)	57 (5)	54 (5)	45 (11)	26 (10)	20 (9)
C2	65 (6)	41 (4)	48 (4)	-5 (8)	29 (8)	-7 (7)
C3	92 (8)	113 (9)	91 (7)	87 (15)	58 (12)	-61 (14)
C4	65 (7)	83 (7)	81 (6)	18 (11)	-37 (11)	-19 (11)
C5	116 (10)	77 (7)	118 (9)	89 (14)	72 (15)	96 (13)
C6	151 (12)	189 (14)	67 (7)	153 (22)	83 (15)	128 (16)
C7	119 (8)	76 (6)	32 (4)	10 (13)	31 (9)	12 (9)
C8	57 (6)	42 (4)	45 (4)	9 (8)	38 (8)	-5 (7)
C9	87 (7)	65 (6)	46 (4)	-12 (10)	56 (9)	-5 (8)
C10	101 (8)	68 (6)	50 (5)	-12 (11)	60 (11)	-13 (9)
C11	68 (7)	57 (5)	58 (5)	5 (10)	13 (9)	-19 (9)
C12	88 (7)	53 (5)	62 (5)	-17 (10)	49 (10)	-5 (9)
C13	85 (7)	44 (5)	55 (5)	-16 (9)	54 (10)	3 (8)
C14	73 (7)	42 (4)	68 (5)	-6 (9)	83 (10)	6 (8)
C15	71 (7)	69 (6)	61 (5)	15 (10)	50 (10)	39 (9)
C16	94 (8)	86 (7)	77 (6)	47 (12)	83 (12)	53 (11)
C17	97 (8)	68 (6)	120 (8)	35 (12)	137 (15)	54 (11)
C18	108 (10)	79 (8)	148 (10)	1 (14)	155 (7)	-56 (14)
C19	114 (9)	58 (6)	122 (8)	22 (12)	143 (15)	-57 (11)

^a The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

largest shift of any parameter in the last cycle was less than one-eighth of a standard deviation; therefore the refinement was considered completed.

Atomic scattering factors for Pd, S, and N were taken from ref 12 and for P and C from hfs wave functions.¹³ Because of the variation in reported values for the $\Delta f'$ correction for Pd for Cu $K\alpha$ radiation,¹²⁻¹⁴ no disper-

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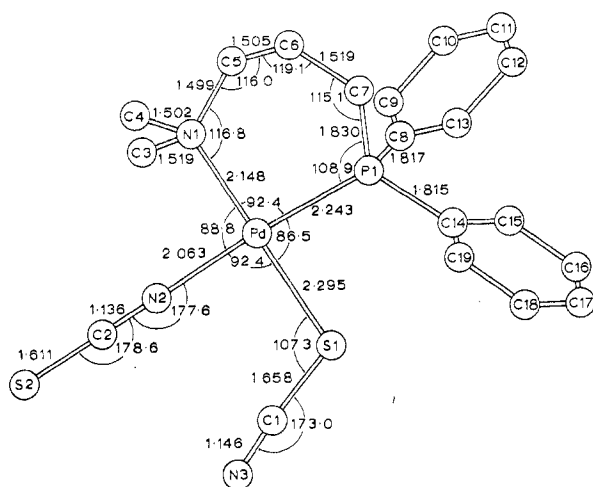


Figure 1.—Idealized view of the molecule of $\text{Pd}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2](\text{SCN})(\text{NCS})$ with pertinent distances (\AA) and angles (deg). The average estimated standard deviations for bond distances and angles are given in Table IV.

TABLE IV

BOND DISTANCES (\AA) AND BOND ANGLES (deg) NOT SHOWN IN FIGURE 1, TOGETHER WITH A SUMMARY OF THE AVERAGE ESTIMATED STANDARD DEVIATIONS OF DISTANCES AND ANGLES

Bond	Angle	Angle	Bond	Angle	
C8-C9	1.401	C9-C8-C13	120.3	C15-C14-C19	121.4
C8-C13	1.387	C8-C9-C10	119.1	C14-C15-C16	119.5
C9-C10	1.387	C9-C10-C11	121.0	C15-C16-C17	118.6
C10-C11	1.381	C10-C11-C12	119.6	C16-C17-C18	122.2
C11-C12	1.404	C11-C12-C13	119.9	C17-C18-C19	118.6
C12-C13	1.383	C8-C13-C12	120.2	C14-C19-C18	119.6
		P1-C8-C9	119.5	P1-C14-C19	118.4
		P1-C8-C13	120.2	P1-C14-C15	120.1
C14-C15	1.399	Pd-P1-C14	116.8	C3-N1-C4	107.6
C14-C19	1.396	Pd-P1-C8	114.4	C3-N1-C5	105.9
C15-C16	1.412	C7-P1-C14	104.8	C4-N1-C5	110.6
C16-C17	1.402	C7-P1-C8	107.2	Pd-N1-C3	105.4
C17-C18	1.396	C8-P1-C14	104.0	Pd-N1-C4	109.9
C18-C19	1.413	S-Pd-N1	176.1	P1-Pd-N2	178.5
Bond	σ , \AA	Bond	σ , \AA	Bond	σ , \AA
Pd-S or -P	0.002	S-C	0.008	N-C	0.011
Pd-N	0.007	P-C	0.007	C-C	0.012
Angle	σ , deg	Angle	σ , deg	Angle	σ , deg
Pd-S-C	0.3	S-Pd-P	0.07	S-C-N	0.8
Pd-P-C	0.2	S-Pd-N	0.2	P-C-C	0.6
Pd-N-C	0.5	P-Pd-N	0.2	N-C-C	0.9
C-P-C	0.4	N-Pd-N	0.2	C-C-C	0.8
C-N-C	0.7				

distance in the literature) is longer than the value found in the present study. The lack of data precludes any definitive comments. However, the Pd-S bond distance is consistent with the values reported in methioninepalladium(II) chloride of $2.28 \pm 0.01 \text{ \AA}$,¹⁸ in bis(dimethyl sulfide)palladium(II) bromide of 2.30 \AA ,¹⁹ and in *trans*-dichlorobis(dimethyl sulfoxide)palladium(II).²⁰ The similarity of the Pd-S bond length in these compounds is surprising since the hybridization of the

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sulfur atom is different in some of the molecules. Additional structural studies on palladium compounds containing sulfur and phosphorus atoms would be useful for interpreting the observed distances.

The Pd-N distances are longer than the values recently reported in bis(3-hydroxy-1,3-diphenyltriazine)palladium(II) of 1.99 \AA ,²¹ in bis(ethylenediamine)palladium(II) chloride of $2.036 \pm 0.007 \text{ \AA}$,²² in bis(*N*-isopropyl-3-methylsalicylaldiminato)palladium(II) of $2.031 \pm 0.002 \text{ \AA}$,²³ in tetragonal bis(*N*-isopropyl-3-methylsalicylaldiminato)palladium(II) of $2.032 \pm 0.003 \text{ \AA}$,²⁴ in methioninepalladium(II) chloride of $2.07 \pm 0.01 \text{ \AA}$,¹⁸ in bis(2-thioimidazolidine)palladium(II) thiocyanate of $1.99 \pm 0.02 \text{ \AA}$,²⁵ in bis(2,2'-dipyridyliminato)palladium(II) of $2.022 \pm 0.007 \text{ \AA}$,²⁶ and in bis(*N*-*n*-butylsalicylaldiminato)palladium(II) of 2.01 \AA .²⁷ Therefore, a lengthening of the Pd-N bond in isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane)palladium(II) due to a trans effect is consistent with the available structural data.

The dimensions of the thiocyanate group found in various compounds are tabulated in Table VI²⁸⁻³⁶ according to the type of bonding. The two C-N bond distances in the present study are not significantly different from each other and with one exception are not significantly different from the values found in other thiocyanates. The C-N distance of $1.24 \pm 0.02 \text{ \AA}$ reported for ammonium silver dithiocyanate²⁸ appears anomalous compared to the other values.

The C2-N2 distance of $1.136 (10) \text{ \AA}$ appears short relative to the other N-bonded thiocyanates. Whether or not this shortening is related to the effect of the trans phosphorous atom cannot be answered at present. Similarly the S-bonded thiocyanate has longer C1-N3 and C1-S1 distances which again may be related to the N atom being trans to S1. The two C-S bonds found in the present study are significantly different, possibly representing a difference in the hybridization or bonding of the two thiocyanate groups.

The mean-square displacements obtained from the thermal parameters for all atoms are given in Table VII. For the Pd atom the largest displacement is approximately parallel to the normal to the plane (the angle is 21°). In almost all cases considered the mini-

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TABLE V
LEAST-SQUARES PLANES

Coordn square (S1, P1, N1, N2)							
Dev ^a = -0.138X + 0.573Y + 0.808Z - 1.893							
Atom	S1	P1	N1	N2	Pd	S2	N3
Dev, Å	0.043	-0.043	0.045	-0.046	-0.028	-0.120	0.515
Benzene ring 1 (C8, C9, C10, C11, C12, C13)							
Dev ^a = 0.824X - 0.364Y + 0.435Z - 1.178							
Atom	C8	C9	C10	C11	C12	C13	P1
Dev, Å	0.002	0.005	-0.007	0.002	0.004	-0.006	0.088
Benzene ring 2 (C14, C15, C16, C17, C18, C19)							
Dev ^a = 0.357X + 0.718Y - 0.597Z - 3.760							
Atom	C14	C15	C16	C17	C18	C19	P1
Dev, Å	0.001	0.006	0.001	-0.013	0.019	-0.013	-0.059

^a The atom coordinates X, Y, Z are in ångströms expressed in terms of the orthogonal axes a, b, c*.

TABLE VI
BOND DISTANCES AND ANGLES IN THIOCYANATE GROUPS

N-C, Å	C-S, Å	N-C-S, deg	Compound	Ref
(a) Thiocyanate Ions				
1.10	1.71		Ammonium silver dithiocyanate	28
1.149 (14)	1.689 (13)	178.3 (1.2)	Potassium thiocyanate	29
1.179 (13)	1.598 (8)	177.6 (0.4)	4-Phenyl-1,2-dithiolium thiocyanate	30
(b) Metal Isothiocyanates (M-NCS)				
1.159 (27)	1.630 (24)		K ₃ Mo(NCS) ₆ · H ₂ O · CH ₃ COOH	31
1.13	1.65		Bis(hydrazine)zinc isothiocyanate	32
1.169 (16)	1.636 (14)	178.8 (1.2)	trans-Dithiocyanatotetrakis(N,N'-diethylthiourea)nickel(II)	33
1.169 (14)	1.635 (13)	178.8 (1.0)	Bis(2-thioimidazolidine)nickel(II) isothiocyanate	25
1.16 (3)	1.64 (2)	178.0 (2.0)	Bis(thiourea)nickel(II) isothiocyanate	34
1.15 (7)	1.64 (7)	175 (6)	Trimethyltin isothiocyanate	35
1.136 (10)	1.611 (8)	178.6 (0.7)	PNPd(SCN)(NCS)	
(c) Metal Thiocyanates (M-SCN)				
1.24 (2)	1.60 (1)		Ammonium silver dithiocyanate	28
1.16 (3)	1.62 (2)	176.9	Bis(ethylenediamine)copper(II) thiocyanate	36
1.146 (12)	1.658 (8)	173.0 (0.8)	PNPd(SCN)(NCS)	

TABLE VII
MEAN-SQUARE DISPLACEMENTS

Atom	-10 ³ (r ²) ^{1/2} , Å			Atom	-10 ³ (r ²) ^{1/2} , Å		
	161	170	207		C7	181	252
Pd	161	170	207	C7	181	252	278
S1	161	214	307	C8	175	198	207
S2	169	271	289	C9	204	222	241
P1	161	177	198	C10	209	236	259
N1	145	220	265	C11	195	215	268
N2	180	224	258	C12	204	237	250
N3	217	307	334	C13	186	226	236
C1	182	240	263	C14	169	196	258
C2	186	198	220	C15	201	206	271
C3	170	276	370	C16	217	226	311
C4	166	260	350	C17	198	220	350
C5	175	289	363	C18	200	256	389
C6	189	281	444	C19	198	223	358

mum displacement is approximately parallel to the corresponding bond. For S2 the maximum displacements are approximately normal (81 and 83°) to the C2-S2 bond; however, the correction to the C2-S2 bond length is small because the differences in the displacements between C2 and S2 are small. The reasonable nature of the mean-square displacements suggests that absorption effects are not serious.

The three P-C bond distances average 1.821 ± 0.008 Å and agree with distances found in the di- and triphenylphosphines which may be coordinated to a metal (e.g., in diphenylphosphinetetracarbonyliron of 1.820

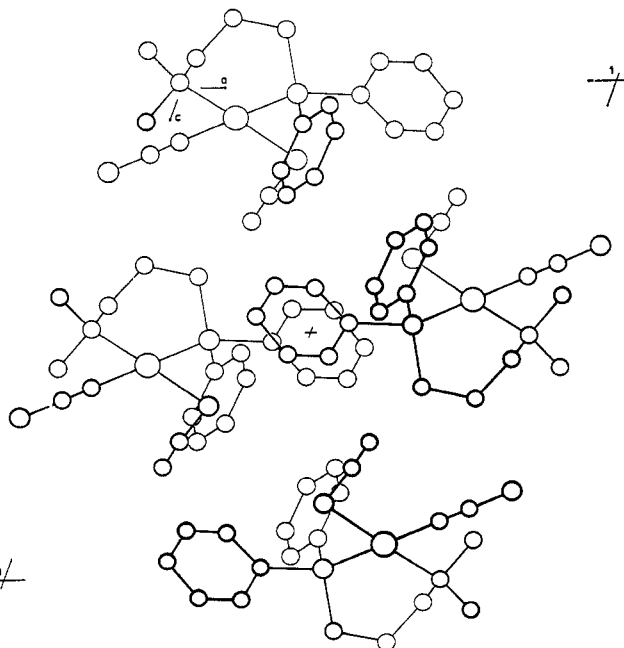


Figure 2.—The molecular packing as seen in the [010] projection.

± 0.007 Å³⁷ or in dibromobis(triphenylphosphine)-nickel(II) of 1.824 ± 0.015 Å³⁸) or uncoordinated (in

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triphenylphosphine of $1.828 \pm 0.005 \text{ \AA}^{89}$). The phenyl rings are planar (see Table V) with average C-C distances of 1.391 and 1.403 \AA in the two rings. The individual distances are given in Table IV. The C-C and C-N distances and the various angles in the ligand chain are close to the expected values.

The packing of the molecules in the unit cell is illustrated in Figure 2. The closest intermolecular approach to a palladium atom is 3.65 \AA from a terminal sulfur atom of an isothiocyanate group. There are six other intermolecular contacts less than 3.6 \AA which can be viewed as van der Waals contacts or slightly longer (see Table VIII). The slight bends at C1 and C2 of the thiocyanate groups may be related to crystal packing. A similar explanation is given for

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TABLE VIII
INTERMOLECULAR CONTACT DISTANCES SHORTER THAN 3.6 \AA

Atom (at x , y , z)	Atom	Posi- tion ^a	Dis- tance, \AA	Atom (at x , y , z)	Atom	Posi- tion ^a	Dis- tance, \AA
S1	C11	-2	3.535	N3	C16	-2	3.498
N3	C4	-1	3.522	C2	C6	2	3.455
N3	C15	-2	3.492	C18	C18	-1	3.528

^a The equivalent transformations are represented by: 1 for x, y, z ; 2 for $x, 1/2 - y, 1/2 + z$; -1 for $-x, -y, -z$; -2 for $-x, 1/2 + y, 1/2 - z$.

similar bends observed in the other thiocyanate complexes (see Table VI) since there are no apparent electronic reasons for deviations from linearity.

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The Crystal and Molecular Structure of *trans*-Chloronitrosylbis(ethylenediamine)cobalt(III) Perchlorate

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The crystal structure of *trans*-[CoCl(NO)(C₂H₈N₂)₂][ClO₄], *trans*-chloronitrosylbis(ethylenediamine)cobalt(III) perchlorate, has been determined by single-crystal X-ray diffractometry at 20°. This complex crystallizes in the monoclinic space group *P*2₁/*c* with $a = 6.636$ (1) \AA , $b = 16.003$ (2) \AA , $c = 12.315$ (2) \AA , and $\beta = 103.74$ (2)°. The structure, including hydrogen atoms, has been refined by least-squares techniques to an unweighted *R* factor of 0.062. The cobalt atom in *trans*-CoCl(NO)(en)₂⁺ is in a distorted octahedral environment formed by the four nitrogen atoms of the ethylenediamine ligands, a chlorine atom, and the nitrogen atom of the NO group. The bent Co-N-O angle of 124.4 (11)° suggests that this complex contains a formally coordinated NO⁻ group. The unusually long Co(III)-Cl distance of 2.575 (3) \AA indicates that the NO⁻ ligand exerts a large structural trans influence which is attributed to its strong σ -donor and weak π -acceptor capacity. In the crystal structure of this complex, there are hydrogen bonds between the ethylenediamine ligands and the oxygen atoms of the ClO₄⁻ ions.

Introduction

Because of its electronic structure NO is a versatile ligand.¹ The majority of nitrosyl complexes are thought to involve σ donation from NO⁺ to the transition metal and an appreciable amount of metal→ligand π back-bonding. This group of nitrosyl compounds is characterized by a linear M-N-O group, a contracted M-N bond length, and an N-O infrared stretching frequency which is usually in the 1750–2000-cm⁻¹ range.

However, examples^{2–4} of complexes containing an NO⁻ group have recently been prepared and found to have several common physical and structural features. The N-O frequencies are in the region of ~1500–

1750 cm⁻¹ and the electronic spectra and magnetic susceptibility indicate an oxidation state of the metal consistent with the presence of a formally coordinated NO⁻ group. Moreover, an M-N-O angle of approximately 120° has been found in the two X-ray structural investigations^{5,6} of this type of nitrosyl. These data suggest that the nitrogen atom of coordinated NO⁻ is sp² hybridized and that less π bonding of the metal-to-ligand type occurs than in complexes involving NO⁺.

In order to determine the structural parameters associated with a bonded NO⁻ group we undertook a study of *trans*-[CoCl(NO)(en)₂][ClO₄] where en is ethylenediamine. This complex is the first six-coordinate compound of this type which has been studied by X-ray methods, and an unexpectedly large structural trans influence of the NO⁻ ligand was found. The preliminary results of this study were reported earlier.⁷

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