would affect both the isomer shift and the splitting.[20] This lends support to the idea that the lowered moment is a result of interaction between ions.

Structure of the SCN⁻ and SeCN⁻ Complexes.—Based on the evidence presented, the proposed structure for $[Fe(phen)_2(SCN)_2]$ is given in Fig. 2. The structures of $[Fe(phen)_2(SeCN)_2]$ and $[Fe(bipy)_2(SCN)_2]$ are assumed to be analogous. From the X-ray evidence, there is no doubt that these are different in structure from the normal bis complexes. The only explanation for the peculiar magnetic results is one based on ion–ion interaction, although the effects are not similar to those observed for known binuclear complexes[10] and we are unable to explain in more detail the exact nature of the interactions or give a more precise interpretation of the data.[21]

The bridge structure in which either sulfur or selenium is bonded to both atoms is favored over the –NCS– bridge for two reasons. First and most important is the fact that the latter type would place the iron atoms at least 5–7 Å. apart, too far for any strong interactions. On the other hand, in the proposed structure the Fe–Fe distance would certainly be less. There is also the possibility of an indirect interaction through the sulfur in the proposed structure. The second point in favor of the sulfur bridge is the infrared results. This is really negative evidence, since the infrared data indicate the absence of a –NCS– bridge, yet the complexity suggests a complex structure.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work under grants NSF-G14529 and NSF-GP1706.

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[20] Unpublished observation. See footnote 19.

[21] It has been pointed out by one of the referees that complexes of higher molecularity cannot be excluded from consideration. We agree, but feel that until more data are available, the binuclear species is most likely.

CONTRIBUTION FROM THE INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY,
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Dielectric Polarization Studies on Cobalt(II) and Cobalt(III) Complexes with Substituted Salicylaldimines[1]

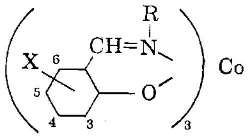
BY M. CIAMPOLINI, F. MAGGIO, AND F. P. CAVASINO

Received March 12, 1964

The molecular polarizations of a number of cobalt(II) and cobalt(III) complexes with substituted salicylaldimines are reported. The values of the electric dipole moments show that the cobalt(III) compounds have the *trans*-octahedral configuration.

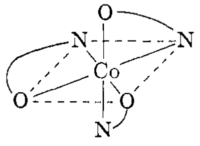
Introduction

In recent years diverse complexes of cobalt(III) with N-substituted salicylaldimines of the general formula

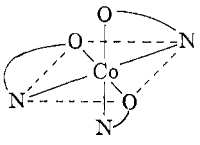


I

($X = H$; R = *n*-alkyl,[2–4] aryl,[2,3] benzyl,[2,3] phenylethyl[2]) have been prepared and studied. The asymmetry of these bidentate ligands makes possible the existence of *cis* and *trans* geometrical isomers of the octahedral cobalt(III) complexes with the configurations



cis



trans

However, only one form was isolated in the solid state.[2,3] On the other hand, the robust character of these complexes,[3] as in general with chelate complexes of cobalt(III),[5] allows one confidently to exclude the possibility that the form isolated gives in solution at room temperature a mixture of the two geometrical isomers. On the basis of steric considerations[2,3] and the values of the dipole moments,[2] the *trans*-octahedral structure was tentatively assigned to the isolated complexes.

In order definitely to clarify the problem, the dipole moment measurements have been extended to other compounds of cobalt(III) and cobalt(II) with salicylaldimines. Thus, compounds of the type I in which R = *i*-C_3H_7, *n*-C_3H_7; X = 3-Cl, 5-Cl, 3,4-benzo, 5,6-benzo have been prepared and characterized. The dipole moments of all these complexes have been measured.

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[1] This work was supported by the U. S. Department of the Army through its European Research Office, under contract No. DA-91-591-EUC-2965, and by the Italian Consiglio Nazionale delle Ricerche.

[2] F. P. Cavasino, M. Ciampolini, and F. Maggio, *Atti Accad. Sci., Lettere Arti Palermo*, **20**, Ser. IV, Pt. I, 5 (1960); *cf. Chem. Abstr.*, **57**, 12,086 (1962).

[3] O. West, *J. Chem. Soc.*, 4944 (1960).

[4] H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962).

[5] R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962).

Experimental

Preparation of Compounds.—The compounds of cobalt(II) and cobalt(III) have been prepared according to the methods previously described.[2,6] The cobalt(III) compounds are dark green solids.[2-4] The cobalt(II) complexes are red solids fairly stable to air[6,7]; the derivatives with R = *n*-alkyl are readily oxidized by air when dissolved.

Tris-(3-chloro-N-*n*-propylsalicylaldimino)cobalt(III); m.p. 198–201°. *Anal.* Calcd. for $C_{30}H_{33}Cl_3N_3O_3Co$: N, 6.48; Co, 9.08. Found: N, 6.59; Co, 9.12.

Tris-(5-chloro-N-*n*-propylsalicylaldimino)cobalt(III); m.p. 216–218°. *Anal.* Calcd. for $C_{30}H_{33}Cl_3N_3O_3Co$: N, 6.48; Co, 9.08. Found: N, 6.55; Co, 9.10.

Tris-(3,4-benzo-N-*n*-propylsalicylaldimino)cobalt(III); m.p. 191–194°. *Anal.* Calcd. for $C_{42}H_{42}N_3O_3Co$: N, 6.04; Co, 8.47. Found: N, 6.08; Co, 8.59.

Tris-(5,6-benzo-N-*n*-propylsalicylaldimino)cobalt(III); m.p. 199–201°. *Anal.* Calcd. for $C_{42}H_{42}N_3O_3Co$: N, 6.04; Co, 8.47. Found: N, 6.14; Co, 8.51.

Bis-(3-chloro-N-*n*-propylsalicylaldimino)cobalt(II); m.p. 229–230°. *Anal.* Calcd. for $C_{20}H_{22}Cl_2N_2O_2Co$: N, 6.19; Co, 13.03. Found: N, 6.23; Co, 13.09.

Bis-(5-chloro-N-*n*-propylsalicylaldimino)cobalt(II); m.p. 165–166°. *Anal.* Calcd. for $C_{20}H_{22}Cl_2N_2O_2Co$: N, 6.19; Co, 13.03. Found: N, 6.25; Co, 13.00.

Dipole Moment Measurements.—The dielectric constants of the solutions were determined with an apparatus and cell described in a previous paper.[8] The measurements on the oxidizable cobalt(II) complexes were made in a nitrogen atmosphere.[9] Densities were measured with a pycnometer. The molar polarization of the solute at infinite dilution, $P_{2\infty}$, was determined by the method of Le Fèvre and Vine.[10] Molar refractions for the sodium D-line, RD, were determined experimentally by measuring the refractive indices of the solutions with a Pulfrich–Zeiss refractometer. The molar refractions for the oxidizable *n*-alkyl cobalt(II) chelates were assumed to be equal to those of the α-branched isomers. Values of the dipole moments were calculated by assuming a value of 20% RD for the atom polarization. Such a figure allows for the entire difference $P_{2\infty} - R$D in the case of the *trans*-planar complexes of nickel(II) and palladium(II) with N-*n*-alkylsalicylaldimines.[11]

Results and Discussion

The values of the dipole moments of the complexes of cobalt(III) with some salicylaldimines are reported in Table I. These can be correlated with the stereochemistry of the complexes using a vectorial model. To check the correctness of the model the complexes of cobalt(II) with analogous ligands were also taken into consideration. The cobalt(II) complexes were previously shown to be tetrahedral.[6,7,11] The model we have used is as described below (Fig. 1).

(a) Each group comprising the salicylaldimine residue and the metal ion lies practically in one plane. This is shown by structural determinations by X-ray methods of some metal–salicylaldimine complexes.[12,13]

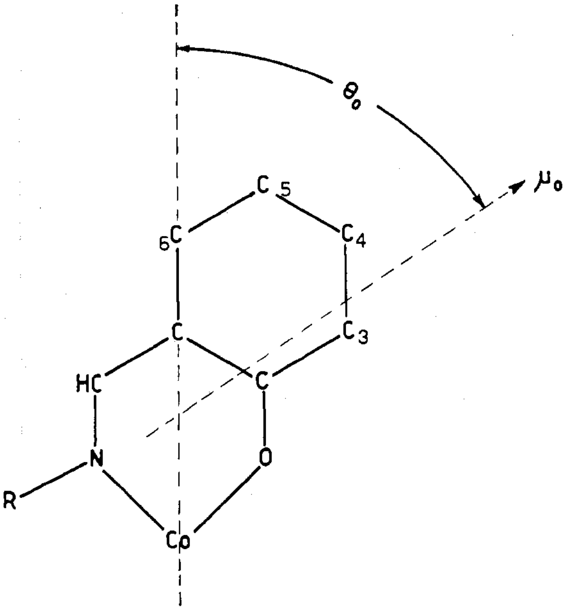

Fig. 1.—Vectorial model for a chelate ring.

TABLE I

DIELECTRIC POLARIZATION DATA FOR SOME COBALT(III) AND COBALT(II) COMPLEXES WITH SALICYLALDIMINES

X	R	$P_{2\infty}$, cc.	RD, cc.	μ, D.
		Cobalt (III)		
H	CH_3[a]	680	141	4.99
	C_2H_5[a]	636	154	4.69
	n-C_3H_7[a]	633	168	4.59
	n-C_4H_9[a]	705	181	4.88
	n-C_5H_{11}[a]	702	195	4.78
	C_6H_5	521	200	3.70
3-Cl	*n*-C_3H_7	1050	197	6.27
5-Cl	*n*-C_3H_7	745	197	4.98
3,4-Benzo	*n*-C_3H_7	638	219	4.28
5,6-Benzo	*n*-C_3H_7	584	219	3.96
		Cobalt(II)		
H	*n*-C_3H_7	591	121	4.67
	i-C_3H_7[b]	594	121	4.69
	n-C_4H_9[b]	594	130	4.62
	s-C_4H_9[b]	595	130	4.63
	t-C_4H_9[b]	679	130	5.05
	n-C_5H_{11}	605	139	4.62
	C_6H_5	525	143	4.16
3-Cl	*n*-C_3H_7	976	131	6.32
	i-C_3H_7[c]	1017	131	6.48
	t-C_4H_9[c]	1144	140	6.90
5-Cl	*n*-C_3H_7	614	131	4.72
	i-C_3H_7[c]	609	131	4.70
	t-C_4H_9[c]	702	140	5.11
3,4-Benzo	*i*-C_3H_7	531	155	4.10
5,6-Benzo	*i*-C_3H_7[c]	513	155	4.00

[a] *Cf.* ref. 2. [b] *Cf.* ref. 9. [c] L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).

(b) The electric dipole moment μ_0 of each group mentioned above (X = H, R = alkyl) lies, for reasons of symmetry, in the same plane as in (a). The angle θ_0 formed between μ_0 and the bisector of the O–Co–N angle is measured in the clockwise direction.

(c) For the tetrahedral structure, the planes of the chelate rings are taken to be mutually perpendicular.

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(6) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

(7) B. O. West, *J. Chem. Soc.*, 1374 (1962); H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. anorg. allgem. Chem.*, **316**, 278 (1962); H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Japan*, **35**, 1430 (1962).

(8) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961).

(9) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963).

(10) R. J. Le Fèvre and H. Vine, *J. Chem. Soc.*, 1805 (1937).

(11) L. Sacconi, M. Ciampolini, F. Maggio, and G. Del Re, *J. Am. Chem. Soc.*, **82**, 815 (1960).

(12) E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959); E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, **14**, 1222 (1961).

(13) M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature* **197**, 1104 (1963).

The bisectors of the two O–Co–N angles are collinear.

(d) For the octahedral structure the planes of the chelate groups are considered to be mutually perpendicular as in a regular octahedron. The three O–Co–N angle bisectors also bisect the corresponding edges of the octahedron and meet each other at angles of 120°.

From the simple calculation of vector addition the dipole moments are, thus: for a tetrahedral compound $|\sqrt{2}\mu_0^{\mathrm{II}}|\sin\theta_0^{\mathrm{II}}|$, for a *trans*-octahedral compound $|\sqrt{2}\mu_0^{\mathrm{III}}|\sin\theta_0^{\mathrm{III}}|$, and for a *cis*-octahedral compound $|\sqrt{6}\mu_0^{\mathrm{III}}|\sin\theta_0^{\mathrm{III}}|$. Therefore, the dipole moment of a *cis*-octahedral compound is $\sqrt{3} = 1.73$ times that of the *trans* isomer. But in the absence of values of the group moments it is impossible to calculate the values of μ_0 and θ_0 for these compounds.

For a compound with a chloro substituent in the benzene ring one has the following.

(e) The dipole moment of the C–Cl bond, $\mu_{\mathrm{C-Cl}}$, being collinear with the bond, lies in the plane of the chelate ring. Its value is 1.58 D. with the negative end of the dipole on the chlorine atom.[14] The angle θ_{X} that the C–Cl bond forms with the bisector of the O–Co–N angle is measured in the clockwise direction. The dipole moment of a chloro-substituted compound is thus: tetrahedral structure

$$|\sqrt{2}(\mu_0^{\mathrm{II}}\sin\theta_0^{\mathrm{II}} + \mu_{\mathrm{C-Cl}}\sin\theta_{\mathrm{X}})|$$

trans-octahedral structure

$$|\sqrt{2}(\mu_0^{\mathrm{III}}\sin\theta_0^{\mathrm{III}} + \mu_{\mathrm{C-Cl}}\sin\theta_{\mathrm{X}})|$$

cis-octahedral structure

$$|\sqrt{6}(\mu_0^{\mathrm{III}}\sin\theta_0^{\mathrm{III}} + \mu_{\mathrm{C-Cl}}\sin\theta_{\mathrm{X}})|$$

For the 3-chloro and 5-chloro derivatives of the cobalt(II) and cobalt(III) complexes with salicylaldimines the geometry of the chelate group, found in the structural investigations already mentioned,[12,13] is such that $\theta_{3\text{-Cl}} = 120°$ and $\theta_{5\text{-Cl}} = 0°$. Inserting these values in the above formula one calculates the difference $\Delta\mu_{\mathrm{X}}$ between the dipole moment of one complex and that of a chloro derivative. The observed and calculated values of the differences are given in Table II. For the tetrahedral complexes of cobalt(II), the observed and calculated values of $\Delta\mu_{5\text{-Cl}}$ are within the experimental error of one another. This proves that the bisectors of the O–Co–N angles are practically collinear. The observed values of $\Delta\mu_{3\text{-Cl}}$ are slightly less than the calculated values but the discrepancies decrease as the alkyl group increases in size, which suggests the structure is more closely tetrahedral, the more bulky is the alkyl group. This can tentatively be attributed to the nonorthogonality of the planes of the two chelate rings as was assumed in (c). Denoting the dihedral angle between the two planes of the chelate rings as φ (measured between the two semiplanes each containing one nitrogen atom) one calculates that

$$|\Delta\mu_{3\text{-Cl}}| = |\sqrt{2(1+\cos\varphi)}\mu_{\mathrm{C-Cl}}\sin\theta_{\mathrm{X}}|$$

The observed values of $|\Delta\mu_{3\text{-Cl}}|$ for R = n-C_3H_7 (1.65 D.), R = i-C_3H_7 (1.79 D.), and R = t-C_4H_9 (1.85 D.) give φ = 106, 98, and 95°, respectively. Unfortunately this hypothesis cannot be fully verified because no complete structural determination of a cobalt(II) complex with a salicylaldimine has been performed. Nevertheless, single crystal measurements on the single complex bis(N-isopropylsalicylaldimino)cobalt(II) have shown it to be practically isometric and so isostructural with the analogous nickel(II) complex.[15] The complete structure of this tetrahedral nickel(II) complex shows that the angle φ is in fact 98°.[13] Such good agreement, however, is partly fortuitous because of the experimental errors and the assumptions implicit in our model.

Table II

Effect of Chloro Substitution in the Salicylaldimine Ring on the Dipole Moments

R	Stereo-chemistry	$\Delta\mu_{3\text{-Cl}}$, D.		$\Delta\mu_{5\text{-Cl}}$, D.	
		Calcd.[a]	Found	Calcd.	Found
		Cobalt(II)			
n-C_3H_7	Tetrahedral	±1.93	−1.65	0	−0.05
i-C_3H_7	Tetrahedral	±1.93	−1.79	0	−0.01
t-C_4H_9	Tetrahedral	±1.93	−1.85	0	−0.06
		Cobalt(III)			
n-C_3H_7	*trans*-Octahedral	±1.93	−1.68	0	−0.39
	cis-Octahedral	±3.34		0	

[a] Negative values for $0 < \theta_0 < 180°$; positive values for $180° < \theta_0 < 360°$.

For the complexes of cobalt(III) the difference, 1.69 D., between the dipole moment of tris(N-n-propylsalicylaldimino)cobalt(III) and that of the 3-chloro derivative is in agreement with the value expected for the *trans*-octahedral configuration. In this case, too, the observed value is slightly less than the calculated one, probably because of deviations from the postulated geometry. In particular, the nonzero effect of substitution in position 5 on the benzene ring leads one to suppose that the angles between the bisectors of the O–Co–N angles are slightly different from those required by condition (d).

Having thus ascertained that these N-n-propyl complexes have the *trans*-octahedral structure we can now calculate the value of $|\mu_0^{\mathrm{III}}\sin\theta_0^{\mathrm{III}}| = \mu/\sqrt{2}$, which is found to be 3.24 D. when R = n-C_3H_7 and X = H. Inspection of Table I shows that the dipole moments of the other tris(N-n-alkylsalicylaldimino)cobalt(III) complexes are very similar to that of compound I (R = n-C_3H_7, X = H). The *trans*-octahedral structure must therefore also be assigned to these complexes, since the dipole moment of the alkyl derivatives depends little on the number of carbon atoms in the alkyl group (*ca.* 0.1–0.3 D.).[16]

An interesting result is that $\mu_0\sin\theta_0$ for the cobalt(II) and cobalt(III) complexes are almost equal. This may perhaps be explained in terms of Pauling's electroneutrality principle,[17] on the basis of which the effective

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[14] J. W. Smith, "Electric Dipole Moments," Butterworths Publications Ltd., London, 1955, p. 96.

[15] L. Sacconi, P. I. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962); L. Sacconi and P. L. Orioli, *Ric. Sci. Rend.*, **32**, 645 (1962).

[16] Reference 14, pp. 89 and 193.

[17] L. Pauling, *J. Chem. Soc.*, 1461 (1948).

charges on the two ions should be equal. In addition, the geometry of the chelate group, in particular the value of the O–Co–N angle, is likely to be the same in both tetrahedral and octahedral complexes. For the complexes of bivalent metals with salicylaldimines it has in fact been shown that the angle O–M–N for the "tetrahedral" complexes is 94°,[13] while for the "square-planar" complexes it is also 94°.[12]

The *trans*-octahedral configuration is also to be assigned to the cobalt(III) complexes with substituted salicylaldimines in which R = C_6H_5, X = H and R = *n*-C_3H_7, X = 3,4-benzo and 5,6-benzo. In fact, the dipole moments of these complexes are very near to those of cobalt(II) with the analogous ligands.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Hexaborane-12 Isolation and Identification[1]

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Hexaborane-12 has been isolated in a good state of purity by application of gas chromatography to separation of the products from several boron hydride interconversions. Vapor pressures, the melting point, an elementary analysis, infrared spectra, and monoisotopic mass spectra are reported, the latter in comparison with hexaborane-10 and pentaborane-11.

Hexaborane appears in several preparations, but in traces, as first found by Stock,[3] who was prevented by the low plate efficiency of fractional condensation from separating cleanly the substance (B_6H_{12}?). The compound has been identified mass spectrometrically in admixture with hexaborane-10 among products from silent discharge treatment of diborane.[4] It has been found as an intermediate in the shock-tube pyrolysis of diborane[5] and as one product from the treatment of the triboranate anion with acid.[6]

In this laboratory B_6H_{12} was collected by g.l.c. separation in trace amounts from several boron hydride interconversions until a sufficient quantity became available to determine the properties reported here.

Experimental

Vacuum line operations used were those developed by Stock[7] and by Schlesinger and his co-workers and described by Sanderson.[8] The g.l.c. separations were carried out on apparatus designed, constructed, and operated as previously described[9,10] with the helium carrier gas vented at atmospheric pressure. At 25° the relative retention times were: B_2H_6, 11; B_4H_{10}, 34; B_5H_9, 100; B_5H_{11}, 124; B_6H_{12}, 330; B_6H_{10}, 500. A column 35 cm. long × 0.6 cm. diameter charged with mineral oil on firebrick completely resolved the two hexaboranes.

The infrared spectrum was obtained on a Perkin-Elmer Model 21 spectrometer with sodium chloride optics, a 5-cm. cell path, and a gas pressure of about 2 cm. Atmospheric absorption peaks were used for calibration to establish the scale within 5 cm.$^{-1}$.

The mass spectra were obtained with a Consolidated Model 20-103 mass spectrometer using a rhenium filament. To ensure a faithful cracking pattern the instrument was checked with pentaborane-11[10] before each run. Ionizing voltages of 70 and 8–14 v. were used. Owing to the uncertainty often experienced in observing mass spectra of certain boron hydrides at the full ionizing potential, 70 v., mass spectra from triplicate samples of hexaborane-12 were given rough statistical analysis with the finding that the standard deviation from the mean abundance for each mass number was ±2.5% for forty mass numbers. The isotopic ratio B^{11}/B^{10} = 4.00 was used, as is customary,[11] to reduce the polyisotopic abundances to the monoisotopic values. The residuals were calculated for the monoisotopic reduction using the formula $R = (\Sigma N_i^2)^{1/2}/\Sigma I$, where R is the residual, N_i is the residue for the ith group, and I, the intensity, is summed over all the abundances.

Hexaborane-12 was obtained in yields of about 1% of the boron in the following reactions: (1) preparation of pentaborane-11 from tetraborane and diborane in a static system at 110° for 10 min.; (2) reaction of tetraborane and diborane and the pyrolysis of tetraborane in the hot–cold reactor[12] with the hot side at 110° and the cold side at 0°; (3) the decomposition of liquid pentaborane-11 at 25°, the easiest systematic method. The large excess of pentaborane-11 over products makes a quantitative determination of yield impossible. Gas chromatographic assay showed about 12% of starting material to disappear in 3 hr. Diborane, tetraborane, and hexaborane-12 appeared in amounts of about 2, 3, and 1.5%, respectively. Initial addition of an equivalent amount of diborane at 10 atm. pressure increased the tetraborane and hexaborane-12 yields inappreciably. No hexaborane-12 was

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[1] Financed by Grant AF-AFOSR-102-63 from the United States Air Force through the Air Force Office of Scientific Research, an assistance gratefully acknowledged. Reproduction for any purpose of the United States Government is permitted.

[2] Postdoctorate fellow, 1962–1963.

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