than the 365 $m\mu$ (singlet → singlet) absorption band for the compound. The maxima correspond quite well with the previously observed vibrational structure of the singlet → triplet transition of phenazine in methyl iodide at 655, 625, 588, 545, and 510 $m\mu$.[8] For polystyrene film a magnetic rotation maximum was observed at 335 $m\mu$, quite close to the triplet-state absorption region for toluene at 347 $m\mu$.[9]

With polymethylmethacrylate, a normal Faraday effect was obtained; however, no magnetic rotation peaks were observed at wave lengths longer than 360 $m\mu$. The above results demonstrate that magnetic rotatory dispersion measurements are useful for detecting the triplet states of certain molecules. A literature search showed that the use of magnetic rotations to detect triplet states is inherent in the theory of the Faraday effect[10] for diatomic molecules. Some experimental evidence for this has been obtained for such molecules as I_2,[11] ICl and IBr.[12] This communication illustrates that the method is also applicable to certain organic compounds and polymers. We are now engaged in examining the scope and utility of magneto-optical rotation spectroscopy.[13]

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[8] R. W. Harrell, Ph.D. Thesis, Florida State University, Tallahassee, Florida, January, 1959.

[9] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

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[13] The author wishes to thank Drs. H. Kobsa and R. W. Harrell of the Du Pont Company for helpful discussions.

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A NEW TYPE OF ALUMINUM HYDRIDE ADDUCT

Sir:

The Lewis adduct between N,N,N',N'-tetramethylethylenediamine and aluminum hydride, which we have recently prepared, probably constitutes the first example of chelation in compounds of this type. This substance, in addition to being thermally more stable than any previously prepared adduct of aluminum hydride, yields information which may have important consequences affecting the structures of all di-adducts of aluminum hydride.

The new compound has been prepared by two procedures, the first of which involved the action of the diamine dihydrochloride on lithium aluminum hydride in an excess of the diamine as a solvent.[1] However, a more convenient route

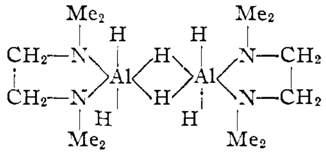
$$2LiAlH_4 + Me_2NCH_2CH_2NMe_2\cdot 2HCl \xrightarrow{Me_2NCH_2CH_2NMe_2} 2H_2 + 2LiCl + 2H_3Al\cdot Me_2NCH_2CH_2NMe_2$$

involved treatment of bis-(trimethylamine)-aluminum hydride with an excess of the tertiary diamine at room temperature. In one such preparation,

$$AlH_3\cdot 2NMe_3 + Me_2NCH_2CH_2NMe_2 \longrightarrow 2NMe_3 + AlH_3\cdot Me_2NCH_2CH_2NMe_2$$

carried out in a tensimeter, 0.473 mmole of $AlH_3\cdot 2NMe_3$ was found to absorb 0.467 mmole of the diamine and, simultaneously, to release 0.949 mmole of trimethylamine.

The adduct prepared in the above manner was a white solid whose vapor pressures at 99.3° and 119.2° were 1.5 mm. and 10.6 mm., respectively. When a sample prepared using 0.20 mmole of $AlH_3\cdot 2NMe_3$ as a starting material was completely vaporized at 125°, 0.101 mmole of vapor was found to be present. This indicates that the diamine adduct in question is a dimer. We feel that dimerization occurs through hydrogen bridging, rather than through the difunctional amine, and propose the structure



Each of the aluminum atoms is 6-coördinate, probably with an octahedral configuration.

Infrared spectra of $AlH_3\cdot 2NMe_3$ and of $(AlH_3)_2\cdot(Me_2NCH_2CH_2NMe_2)_2$ both show identical Al–H stretch absorptions at 5.90μ, from which one is tempted to infer that the two substances have closely related structures, and, particularly, that $AlH_3\cdot 2NMe_3$ is dimeric in the vapor phase. (Determining the molecular size of $AlH_3\cdot 2NMe_3$ directly by tensimetry is not convenient, owing to the pronounced tendency for this substance to dissociate.) Our proposed structure for this substance makes it unnecessary to invoke a pentacovalency for the aluminum atom.

Unlike other AlH_3 adducts, $(AlH_3)_2\cdot(Me_2NCH_2CH_2NMe_2)_2$ showed no tendency to decompose over a 24-hour period at 133°. At the end of this time the ratio of aluminum to hydrogen liberated on hydrolysis was 1.00 to 3.01.

The authors are grateful to the Office of Naval Research for financial assistance in this program.

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[1] This is a modification of the general method developed by Ruff and Hawthorne (THIS JOURNAL, **82**, 2141 (1960)) for the preparation of amine adducts of aluminum hydride.

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RECEIVED AUGUST 18, 1960

MAGNETIC OBSERVATIONS OF SOME SUBSTITUTED NICKEL(II) SALICYLALDIMINE COMPLEXES

Sir:

Recently Sacconi, *et al.*,[1,2] have reported magnetic moments (0.5–1.6 B.M.) of N-alkylsalicylaldimine Ni(II) complexes over a temperature range in the fused state and in dibutyl phthalate solution. They interpret their results in terms of a distribution of individual planar molecules over low-lying singlet and triplet states,[3,4] thus accounting for the partial paramagnetism. This anomalous magnetic behavior whereby certain apparently

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[1] L. Sacconi, R. Cini, M. Ciampolini and F. Maggio, THIS JOURNAL, **82**, 3487 (1960).

[2] L. Sacconi, R. Cini and F. Maggio, *ibid.*, **79**, 3933 (1957).

[3] C. J. Ballhausen and A. D. Liehr, *ibid.*, **81**, 538 (1959).

[4] G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

quadricoördinate Ni(II) complexes, diamagnetic as solids, become partially paramagnetic when dissolved in non-coördinating solvents is now well documented in the case of the salicylaldimines.[5,6,7,8] A second interpretation of the phenomenon as a conformational equilibrium between planar and tetrahedral forms[5,6,7] now may be safely ruled out in view of dielectric polarization data[8] and because the magnetic and, more especially, the spectral properties of the salicylaldimine complexes in this and other work[5,6,7,8] bear no resemblance to recent observations of tetrahedral Ni(II) complexes in which the symmetry is nearly tetrahedral[9] or markedly lower.[10]

We wish to report results for certain N–R salicylaldimine complexes (R = substituent) which indicate that at least in certain instances intermolecular association is a strong contributing factor to partial paramagnetism in solution. Heretofore the magnetic behavior had been attributed to changes in intrinsic ligand field strengths upon dissolving[3] and to solvation.[4] Previous magnetic studies have been carried out in which R = alkyl,[1,2,5,6,7,8] commonly methyl.[5,6,7,8] When R = Et (I), *n*-Pr (II), *n*-Bu (III), we find in benzene and chloroform (in accord with Sacconi[8]) that the nickel is feebly paramagnetic at 300°K. and monomeric or very slightly associated in freezing benzene, but when R = *i*-Pr (IV), *sec*-Bu (V), cyclopentyl (VI), the complexes are strongly paramagnetic in solution and associated. The following results were obtained in benzene at comparable concentrations. Polymerization, however, does not necessarily account fully for the observed paramagnetism. Association may occur via weak Ni...O interactions, analogous to those found in Cu(II) dimethylglyoxime[11] and bis-(salicylaldehyde)-ethylenediimine Cu(II),[12] which provide a tetragonal ligand field component, thus enhancing the triplet character of the ground state.[4] Similar conclusions have been drawn concerning the magnetic properties of certain substituted Ni(II) acetylacetonates.[13]

	μ (B.M.)	Mol. wt. Calcd.	Mol. wt. Found
I	0.23	355	359
II	0.29	383	384
III	0.45	411	435
IV	2.18	383	527
V	2.10	411	501
VI	2.58	435	~640

It was postulated[14] that if spin-free planar Ni(II) complexes do exist, it might be possible to alter singlet–triplet distributions at a given temperature in complexes of the type Ni–O_2N_2. Accordingly, we have prepared and examined an extensive number of N-substituted salicylaldimine complexes. We have found that by altering R it is possible in certain instances to transform the nickel from a predominantly triplet to an essentially singlet state in benzene and chloroform solutions at room temperature. In chloroform when R = C_6H_5 (VII), *p*-C_6H_4F (VIII), *p*-C_6H_4Cl (IX), *p*-tolyl (X), *m*-tolyl (XI), the magnetic moments (25–28°) are: VII, 2.92; VIII, 2.93; IX, 2.91; X, 3.05; XI, 3.25 B.M. However, where R = *o*-tolyl (XII) and 1,5-$C_6H_3(CH_3)_2$ (XIII) the moments are XII, 0.95; XIII, 0.20 B.M. Similar results were obtained in benzene, *e.g.*, VII, 3.08; VIII, 3.04; X, 3.14; XI, 3.26; XII, 0.96, XIII, 0.30 B.M. The ground state is predominantly a triplet[15] in VII–XI, essentially a singlet in XII, and nearly a pure singlet in I–III, XIII. Such large variations in the moments of salicylaldimine complexes or other magnetically anomalous Ni(II) complexes have not been observed previously. The extent to which association affects these variations is being investigated.

A more detailed report of magnetic and spectral studies of these and other Ni(II) salicylaldimine complexes will be the substance of a later communication.

Financial support under grant NSF-G12312 was provided by the National Science Foundation to whom grateful acknowledgment is made.

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[13] J. P. Fackler, Jr., and F. A. Cotton, THIS JOURNAL, **82**, 5005 (1960).

[14] R. H. Holm, *Ibid.*, **82**, Nov. 5 (1960).

[15] Orbital contributions in spin-free planar monomeric Ni(II) complexes are not known but may be estimated as 0.3–0.6 B.M.

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PATHWAY OF PROGESTERONE OXIDATION BY CLADOSPORIUM RESINAE

Sir:

The ability of various microörganisms to cleave oxidatively the side-chain of C_{21} steroids to give C_{19} steroids having a 17-ketone, 17β-alcohol, or a ring D lactone function is well-known.[1] A reasonable path for this type of oxidation of progesterone would appear to be: progesterone → testosterone → androst-4-ene-3,17-dione → testololactone.[2] More recently Sebek, *et al.*,[3] have suggested that *Penicillium lilacinum* Thom degrades progesterone by the path: progesterone → 20β-hydroxypregn-4-en-3-one → testosterone → androst-4-ene-3,17-dione → testololactone.

We have found that incubation of progesterone aerobically[4] with *Cladosporium resinae*[5] affords

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