the infrared and mass spectra with those of the natural product.[7]

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DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY   JAMES A. MARSHALL
STANFORD, CALIFORNIA   WILLIAM S. JOHNSON

NICKEL–NICKEL BOND IN NICKEL DIMETHYLGLYOXIME[1]

Sir:

Godycki and Rundle[2] postulated that nickel–nickel bonding is a fundamental feature of the nickel dimethylglyoxime, [Ni(DMG)$_2$], crystal and that this feature offered an explanation of the great difference in the aqueous solubility of the nickel and copper dimethylglyoxime, [Cu(DMG)$_2$], complexes. From the heats of solution of Ni(DMG)$_2$ and Cu(DMG)$_2$ in n-heptane, Fleischer[3] concluded that the crystal energy of the latter may be greater than that of the former by 2 to 3 kcal. and that if a nickel–nickel bond does exist in the crystal, it would have to be extremely weak.

and the nickel–nickel distance (4.75 Å.) is so great that nickel–nickel bonding is not possible. Also the distance between the nickel and the closest oxygen of an overlying molecule is much too great (3.44 Å.) to involve coördination.

This suggests that a study of the heats of solution of Ni(DMG)$_2$ and Ni(EMG)$_2$ in non-coördinating solvents such as n-heptane and carbon tetrachloride would give a measure of the relative stabilities of these two crystals and, in fact, might give a good measure of the strength of the nickel–nickel bond in Ni(DMG)$_2$.

Saturated solutions of the nickel(II)-vic-dioxime complexes in n-heptane and carbon tetrachloride were prepared at various temperatures. The solubility in n-heptane was so low that it was necessary to extract the nickel into an aqueous hydrochloric acid solution, adjust the pH to 6–7, add additional ethylmethylglyoxime, and concentrate the Ni(EMG)$_2$ by reextraction into chloroform.[7] The absorbancies were measured in the chloroform at 328 mμ. The solubility of Ni-(DMG)$_2$ in carbon tetrachloride was determined by the extraction procedure outlined above. The absorbancies were measured in chloroform at 374 mμ. The solubility of Ni(EMG)$_2$ was determined directly by measuring the absorbancies in the carbon tetrachloride at 378 mμ. Concentrations were obtained by comparison with calibration curves.

The heats of solution were calculated from the temperature dependence of the solubility. The standard state for the solute was taken as the hypo-

TABLE I
THERMODYNAMIC QUANTITIES FOR THE SOLUBILITY OF Ni(DMG)$_2$ AND Ni(EMG)$_2$

Solvent	Complex	\-log X_2 at °C. 25	33.3	35	$\Delta H°$, kcal.	$\Delta F°$, kcal.	ΔS,[b] e.u.
n-Heptane	Ni(DMG)$_2$	7.44[a]		7.08[a]	15.1	10.15	16.62
	Ni(EMG)$_2$	6.74	5.62		5.8	9.19	−11.39
CCl$_4$	Ni(DMG)$_2$	6.24	5.92		15.3	8.50	22.8
	Ni(EMG)$_2$	4.10	4.03		4.0	5.59	−5.34

[a] Values taken from Fleischer.[3]   [b] Calculated for 25°.

Frasson, Bardi and Bezzi[4] have shown that in Cu(DMG)$_2$ the copper is bonded to four nitrogen atoms and with an oxygen atom in a nearby molecule forming a dimer. Dyrssen and Hennichs[5] in a very recent study of the solubilities of the nickel and copper complexes of dimethylglyoxime have concluded that the crystal energies must be about the same and that the large difference in water-solubility must be due to the greater tendency of the Cu(DMG)$_2$ to become solvated, perhaps forming Cu(DMG)$_2$·H$_2$O in aqueous solution.

Frasson and Panattoni[6] have shown that in nickel ethylmethylglyoxime, [Ni(EMG)$_2$], the packing system is completely different from that in Ni(DMG)$_2$. In fact, the nickel–nickel direction is not perpendicular to the plane of the molecule

thetical mole fraction, X_2, of one and 298°K. (Table I).

The $\Delta H°$ values in Table I show that the crystal energy of Ni(DMG)$_2$ is about 9 to 11 kcal. more stable than that of Ni(EMG)$_2$. In view of the X-ray crystal structure studies,[1,4] and the observations that such properties of these complexes as the "abnormal" dichroism,[8] solubility product,[9] and intrinsic solubility[10] correlate rather well with the metal–metal distances in these complexes, it seems reasonable to attribute a large part of this great difference in the crystal energies to the presence of nickel–nickel bonding.

It now appears that Ni(DMG)$_2$ is less soluble in water than Ni(EMG)$_2$ because of the increased stability arising from the nickel–nickel bonding in the crystalline state of the former complex, whereas Ni(DMG)$_2$ is less soluble in water than

(1) Contribution No. 1117. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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Cu(DMG)$_2$ because the latter complex has a much greater tendency to hydrate as it dissolves.

INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY   CHARLES V. BANKS
IOWA STATE UNIVERSITY   SAMUEL ANDERSON
AMES, IOWA
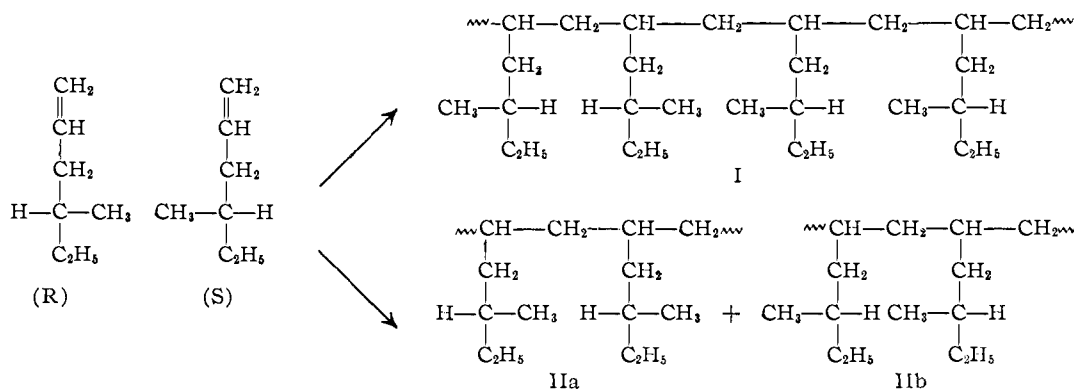
OPTICALLY ACTIVE VINYL POLYMERS. VI. CHROMATOGRAPHIC RESOLUTION OF LINEAR POLYMERS OF (R)(S)-4-METHYL-1-HEXENE

Sir:

Optically active polyhydrocarbons have been prepared up to now by polymerizing optically active[1,2] or racemic monomers,[3] or by polymerizing monomers which do not contain asymmetric carbon atoms in the presence of optically active catalysts.[4]

Recently we have interpreted[5] the fact that the crystalline structure of the polymers of (S)-4-methyl-1-hexene and of (R)(S)-4-methyl-1-hexene are identical, as indicating that the poly-4-methyl-1-hexene obtained from the racemic monomer is not a random copolymer of the two enantiomeric monomers [poly-(R)(S)-4-methyl-1-hexene, (I)], but it is actually a mixture of two types of macro-molecules: the first originating predominantly from the (R) enantiomer and the second from the (S) enantiomer [(R)(S)-poly-4-methyl-1-hexene, (IIa) + (IIb)].

TABLE I

CHROMATOGRAPHIC RESOLUTION OF RACEMIC POLY-4-METHYL-1-HEXENE.[a] SUPPORTING MEDIUM: CRYSTALLINE (+)POLY-(S)-3-METHYL-1-PENTENE[b,c]

Fraction	Eluent	T, °C.	Fraction weight, g.	α^{40}_D ($l = 2$) in benzene solution	$[\alpha]^{40}_D$
1	1:1 acetone diethyl ether mixture	25	0.0364	−0.175°	−23.0°
2	Diisopropyl	25	.0170	− .035°	−13.6°
3	ether	56.2	.0348	− .055°	− 6.7°
4	Diisopropyl	56.2	.0466	− .040°	− 4.1°
5	ether	56.2	.0154	+ .015°	+ 4.8°
6	Benzene	64.5	.0322	+ .185°	+25.0°
7	Benzene	77.1	.0162	+ .155°	+47.7°

[a] A diethyl ether insoluble, diisopropyl ether soluble fraction having [η] 0.92 at 120° in tetralin. [b] Boiling decalin insoluble fraction. [c] Weight of supporting polymer/weight of supported polymer = 30.4; supported polymer 0.22 g.; total polymer eluted 0.1986 g.

lateral chains using, as chromatographic support, an optically active isotactic poly-α-olefin which is insoluble in the eluting solvents.

A partial resolution of a diethyl ether insoluble, diisopropyl ether soluble fraction of the polymer of the racemic 4-methyl-1-hexene[5,7] has been obtained by supporting the racemic polymer on a sample of highly crystalline poly-(S)-3-methyl-1-pentene, (III),[5] which is insoluble not only in the

It should thus be possible, in principle, to resolve the polymer of the racemic 4-methyl-1-hexene into fractions having opposite signs of rotation; the resolution of the racemic polymer should provide a new method for preparing optically active polyhydrocarbons.

Separations of polymers having different steric structures (*e.g.*, isotactic and syndiotactic polypropylene) have been carried out successfully by chromatographic methods.[6] We have therefore tried to resolve some isotactic and block poly-α-olefins with asymmetric carbon atoms in the

eluting solvents used, but also in boiling decalin. The supported polymer has been successively eluted with acetone and diethyl ether at room temperature, diisopropyl ether at room temperature and at 56.2°, benzene at 64.5° and benzene at 77.1° (Table I).

By the same method, acetone or diethyl ether soluble fractions of the racemic poly-3-methyl-1-pentene[5] have been resolved.

As shown in Table II, under comparable conditions the resolution increases with the stereoregularity (*i.e.*, melting point) of the fraction to be resolved.

In all the experiments the first fractions have negative optical rotation, while the last fractions have positive optical rotation. According to the relationship between optical rotation sign and the absolute configuration of the asymmetric carbon

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