

ride favors formation of *exo*- over *endo*-norbornyl chloride by a factor of about 20.<sup>8b</sup> The steric effect of the *syn*-7-methyl group in **2** considerably reduces the rate of *exo* exchange and shows a much smaller effect on the *endo* rate, but as already has been observed qualitatively, there is still a residual preference for *exo* exchange.<sup>4a,c</sup>

The low reactivity of **3** relative to **1** is contrary to the report<sup>4b</sup> of previous authors (who used somewhat different conditions), and the similarity of the *exo:endo* rate ratios of **1**, **3**, and **4** shows that the steric effect of the *endo*-5,6 hydrogens in **1** is not the dominant factor governing its reactivity relative to **3** and **4**. By careful control of the reaction conditions, it has been found possible to selectively deuterate **3** in the *exo* position.<sup>9</sup> Similarly, **4** can be prepared with predominant *exo*-deuterium substitution<sup>11</sup> despite previous<sup>12</sup> intimations to the contrary.<sup>13</sup>

The differences in reactivity among **1**, **3**, and **4** likely reflect the simultaneous operation of a number of effects. Variations in the geometry of the ketones that lead to decreasing internal bond angles would impair enolate formation by increasing the strain in the sp<sup>2</sup>-hybridized intermediates, while the same decrease in internal angles would tend to increase the acidity of the protons due to the increased s character of the external orbitals.<sup>14</sup> Results with cyclopropyl ketones suggest that the former effect is dominant.<sup>2a,b,f</sup>

Homoallyl<sup>15</sup> and homobenzyl<sup>16</sup> stabilization would have been expected to accelerate the rate of anion formation from **3** and **4**, respectively, as would the inductive effect<sup>2g</sup> of the unsaturated groupings. More extensive delocalization to give the "antiaromatic" bishomocyclobutadiene-type of structure would have been destabilizing.<sup>17,18</sup>

(9) Dehydronorcamphor (**3**) (0.112 g) was dissolved in 10 ml of a 0.0363 *N* solution of NaOD in 2:1 dioxane-D<sub>2</sub>O and was maintained at 25° for 55 hr. The reaction mixture was poured into a solution of 5 ml of 0.25 *N* HNO<sub>3</sub>, 25 ml of water, and 25 ml of pentane and after extraction into pentane, the ketone was purified by gas chromatography. The mass spectrum of the ketone indicated 1% *d*<sub>0</sub>, 94% *d*<sub>1</sub>, and 5% *d*<sub>2</sub> species. Reduction of the deuterated ketone with lithium aluminum hydride and purification by vpc gave *endo*-bicyclo[2.2.1]hept-5-en-2-ol whose nmr spectrum showed the complete absence of the heptet assigned<sup>10</sup> to the *exo*-3 H at  $\delta$  1.97 (CCl<sub>4</sub>) and the collapse of the couplings of this proton.

(10) J. C. Davis, Jr., and T. V. Van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965).

(11) Benzodehydronorcamphor (**4**) (0.233 g) was treated as above with a reaction time of 2 hr. The mass spectrum of the purified ketone indicated 2% *d*<sub>0</sub>, 97% *d*<sub>1</sub>, and 1% *d*<sub>2</sub> species. The nmr spectrum of the corresponding *endo* alcohol showed the complete absence of the heptet at  $\delta$  2.20 in the nondeuterated compound which can be assigned to the *exo*-3 H as above. Norcamphor was monodeuterated under similar conditions. The couplings of the nmr absorption of the *exo*-2 H at  $\delta$  4.08 in the derived *endo* alcohol were not resolved at 60 MHz (*cf.* ref 4a) but at 100 MHz, with irradiation of the bridgehead hydrogens at 2.1, showed a broad doublet with the expected 3 cycle coupling to the *endo*-3 H.

(12) R. Caple, F. M. Hsu, and C. S. Ilenda, *J. Org. Chem.*, **33**, 4111 (1968).

(13) Dr. H. Tanida (private communication) has independently measured the rate of hydrogen exchange of **4** and has not only found a preference for *exo* exchange, but has also prepared specifically *exo*-deuterated **4**.

(14) A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Amer. Chem. Soc.*, **91**, 529 (1969).

(15) For leading references see M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

(16) For leading references see H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *J. Amer. Chem. Soc.*, **91**, 4512 (1969).

(17) The possibility of antiaromatic destabilization of the 7-norbornenyl anion was discussed by R. Breslow, lecture at the 21st Organic Chemistry Symposium, Salt Lake City, Utah, June 1969, Abstracts, p 139; see also, R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).



Thus a variety of factors, including ring strain, homoconjugation, hybridization, steric blocking, inductive effects, and torsional effects<sup>19</sup> apparently contribute to the observed relative reactivities of these ketones. A number of investigations are under way in these laboratories to elucidate the respective contributions of these effects.

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(18) For a possible stabilized bishomocyclobutadienyl dication see J. B. Lambert and A. G. Holcomb, *ibid.*, **91**, 1572 (1969). For contrary evidence in the benzo derivative see H. Tanida and T. Tsushima, *Tetrahedron Lett.*, 3647 (1969).

(19) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967); see, however, the experimental results in ref 1.

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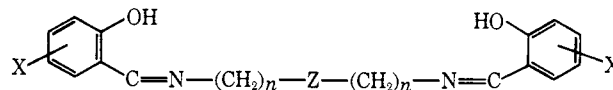
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### A Possible Low-Spin Five-Coordinate Nickel(II) Complex with Predominantly Nitrogen and Oxygen Donor Atoms

Sir:

Five-coordinated nickel(II) complexes may be either diamagnetic or paramagnetic which until recently was thought to depend on the particular donor atoms involved. Ligands with low  $\pi$ -bond-forming ability (*i.e.*, oxygen, nitrogen, etc.) were thought to form only paramagnetic complexes whereas ligands with high  $\pi$ -bond-forming ability (*i.e.*, sulfur, phosphorus, etc.) give rise to diamagnetic complexes.<sup>1</sup>

We wish to report here the synthesis and characterization of a green nickel(II) complex containing a pentadentate ligand which we believe may be the first example of a diamagnetic five-coordinate structure where oxygen serves as two of the donor atoms. Schiff bases formed from substituted salicylaldehydes (X-Sal) and bis(2-aminoethyl) sulfide (DAES) serve as the pentadentate ligand (structure Ia), hereafter referred to as X-SalDAES.



Ia,  $n = 2$ ; Z = S

b,  $n = 3$ ; Z = S

c,  $n = 2$ ; Z = N-H

d,  $n = 3$ ; Z = N-H

(1) L. Sacconi, *Transition Metal Chem.*, **4**, 227 (1968), and references therein.

The metal complexes were prepared by either treating the preformed ligand with nickel(II) acetate tetrahydrate in ethanol or *via* a metal template reaction of the bis(salicylaldehyde)nickel(II) complex with DAES. Complexes of the following composition were isolated, Ni(X-SalDAES). *Anal.* Calcd for Ni(H-SalDAES): C, 56.10; H, 4.93; N, 7.27. Found: C, 56.15; H, 4.78; N, 7.35. In addition to the elemental analyses, infrared and mass spectral data ( $m/e$  413 for Ni(CH<sub>3</sub>-SalDAES)) further corroborate this composition. Magnetic susceptibility measurements of these homogeneous materials at room temperature reveal them to be diamagnetic or weakly paramagnetic, implying either a four-coordinate square-planar environment about the nickel(II) ion in which one of the potential donor sites of the pentadentate ligand is not coordinated or possibly a five-coordinate environment resulting in a low-spin complex. Nujol mull spectra from 20,000 to 3000 Å show single bands in the 16,000-, 22,500-, and 29,500-cm<sup>-1</sup> region. The two lower energy bands are indicative of low-spin five-coordinate nickel(II) complexes.<sup>1</sup>

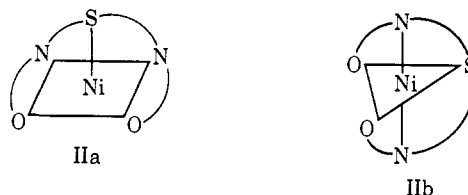
This observation does not, however, prove that the products contain five-coordinate metal ions with a sulfur atom bound in a fifth coordination position. We have, therefore, been studying the nickel(II) complexes of another pentadentate ligand derived from substituted salicylaldehydes and diethylenetriamine (structure Ic), hereafter referred to as X-SalDIEN. These golden yellow complexes have the composition Ni(X-SalDIEN) and are diamagnetic at room temperature with a single band in the visible spectral region at 23,000 cm<sup>-1</sup>. There is little doubt that these complexes are indeed four-coordinate square planar.<sup>2</sup> X-Ray powder patterns of four identical derivatives of both complexes indicate that Ni(X-SalDAES) has a crystal structure unique to that of Ni(X-SalDIEN). Perturbation of the nickel(II) ion in Ni(X-SalDAES) by the sulfur atom is probably responsible for these completely different powder patterns.

Further evidence supporting interaction of the sulfur atom with the nickel ion in some manner is found concerning observations that we have made upon studying the visible spectra of both complexes in pyridine. Band maxima at 10,900 and 17,600 cm<sup>-1</sup> for Ni(X-SalDIEN) and at 10,100 and 17,400 cm<sup>-1</sup> for Ni(X-SalDAES) coupled with the fact that both complexes are paramagnetic as indicated by magnetic susceptibility measurements in solution by an nmr technique<sup>3</sup> strongly suggest that both complexes now possess six-coordinate metal ions in pyridine. If Ni(X-SalDAES) and Ni(X-SalDIEN) were both *cis*-planar NiN<sub>2</sub>O<sub>2</sub> structures, it is anticipated that their spectra in pyridine would give identically positioned band maxima. This is not observed. The lower energy band, which is a measure of the ligand field presented by the donor atoms, is shifted approximately 800 cm<sup>-1</sup> to lower energy for Ni(X-SalDAES) relative to Ni(X-SalDIEN). We feel that this difference can probably be attributed to a NiN<sub>3</sub>O<sub>2</sub>S environment for Ni(X-SalDAES) in pyridine *vs.* a NiN<sub>2</sub>O<sub>2</sub> environment for Ni(X-SalDIEN) in pyridine. The shift to lower energy can be explained

by the fact that a thio ether linkage produces a smaller  $Dq$  than a pyridine nitrogen.<sup>4</sup>

These results may be rationalized in several ways. The sulfur atom because of its orbital extension in space may be perturbing excited states of the molecule without forming a direct ground-state metal-sulfur bond,<sup>5</sup> or production of a five-coordinate species has occurred with formation of a metal-sulfur bond. The postulated five-coordinate Ni(X-SalDAES) may be ideally envisioned to have a square-pyramidal (IIa) or trigonal-bipyramidal (IIb) structure. Dreiding and Fisher-Hirschfelder-Taylor stereomodels do not rule out structure IIa, although structure IIb is reported to be preferred by a somewhat analogous pentadentate ligand, Id.<sup>6</sup> Regardless of the structure, the ligand must undergo severe steric strain in order for the sulfur atom to be situated *near* a coordination site. Consequently, either of the idealized structures is predicted to be highly distorted.

The failure of this ligand to produce a paramagnetic complex can probably be attributed to steric restrictions imposed by the two relatively short ethylene bridges joining the sulfur atom to the two azomethine nitrogens. Because the sulfur atom is forced to take up a position relative to the nickel which is considerably removed from the preferred coordination site, its coordinating tendency is greatly diminished. The diamagnetism arises, therefore, because the weak perturbation is insufficient to unpair the electrons of the nickel(II) ion. A somewhat analogous situation has been reported<sup>7</sup> concerning a nickel(II) complex with a macrocyclic tetradentate ligand possessing four nitrogen donor atoms with an additional coordinated bromide ion. The diamagnetic complex was postulated to be five-coordinate with a water of solvation strongly hydrogen-bonded to the coordinated bromide ion, thereby reducing its coordinating strength. A recent X-ray crystal structure study<sup>8</sup> has confirmed this prediction.



The possible coordination of sulfur in X-SalDAES whereas the secondary nitrogen atom of X-SalDIEN does not coordinate may be rationalized on the grounds that sulfur is a larger atom than nitrogen and is more able to reach and perturb the fifth coordination position about the nickel ion. If the two ethylene carbon chains are increased by one carbon in X-SalDIEN (Id), the nitrogen atom easily reaches the fifth position and gives rise to a high-spin five-coordinate nickel(II) complex.<sup>7</sup> We are presently studying nickel complexes of the sulfur-containing pentadentate ligand with three-carbon chains joining the sulfur atom to the azomethine nitrogen atoms, Ib, in order to test this hypothesis further.

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(5) The comments of the referee are gratefully acknowledged.

(6) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **88**, 5180 (1966).

(7) J. L. Karn and D. H. Busch, *Nature*, **211**, 160 (1966).

(8) E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, **7**, 2312 (1968).

(2) D. H. Busch, *J. Chem. Educ.*, **41**, 77 (1967).

(3) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

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### Increasing Terminal ( $\omega$ ) Chlorination of Fatty Acids by Adsorbing and Aligning the Reactants on Alumina

Sir:

Langmuir showed that fatty acids occupy an area of  $20.5 \text{ \AA}^2$  per molecule when adsorbed on air-water interfaces, independent of chain length or molecular weight.<sup>1</sup> The molecules are aligned with their axis perpendicular to the interface in a close-packed, rigid array. It has no doubt occurred to many chemists that such aligned molecules have their flanks protected and might be selectively attacked on the exposed terminal methyl group. The data in Tables I and II are believed to be the first that demonstrate such an effect.

Table I. Chlorination of Octanoic Acid at 25°

Conditions	% yields of monochlorooctanoic acids							
	2	3	4	5	6	7	8	
Homogeneous ( $\text{Cl}_2$ )	1.5	9	15	15	19	24	17	
5% on alumina ( $\text{Cl}_2$ )	2	4	7	11	22	29	25	
3% on alumina ( $\text{Cl}_2$ )	1	3	5	8	20	30	33	
Homogeneous ( $\text{C}_6\text{H}_6\text{Cl}\cdot$ )		3	14	24	30	26	3	
3% on alumina ( $\text{C}_6\text{H}_6\text{Cl}\cdot$ )		4	12	21	28	30	5	
Homogeneous ( <i>t</i> -BuOCl)	6	7	14	17	22	28	6	
3% on alumina ( <i>t</i> -BuOCl)	6	8	13	14	21	30	8	

Table II. Chlorination of Hexanoic and Butyric Acids

Conditions	% yields of monochloro acids				
	2	3	4	5	6
Hexanoic acid					
Homogeneous ( $\text{Cl}_2$ )	4	13	28	37	18
3% on alumina ( $\text{Cl}_2$ )	1	4	27	36	31
Butyric acid					
Homogeneous ( $\text{Cl}_2$ )	5	53	42		
3% on alumina ( $\text{Cl}_2$ )	1	47	52		

Several problems arose in attempting to use monomolecular films of fatty acids on air-water interfaces so that we turned to  $\text{CCl}_4$ -alumina interfaces in the hope that comparable alignment would obtain. Although the geometries of the alumina-adsorbed acids are not known, they are at least tightly adsorbed. For example, a limiting 7% of octanoic acid was not washed off by methanol.

Chlorination of carboxylic acids was the reaction chosen. Emphasis was placed on octanoic acid. This was a compromise between using carboxylic acids of short enough chain length to facilitate analysis and a long enough chain length to favor alignment. Butyric and hexanoic acids were also studied.

The yield of 8-chlorooctanoic acid is nearly doubled (17-33%) when the octanoic acid is adsorbed on alu-

mina. Of equal importance, the sum of the yields of 7- and 8-chloro increases from 41 to 63% and the yields of 2-5-chloro drops from 40 to 17%. Similar results were obtained with hexanoic and butyric acids (Table II). As anticipated, the effect was smaller with shorter chains in which the London forces favoring rigid alignment have been reduced.

It had been hoped that larger attacking radicals such as the  $\text{C}_6\text{H}_6\text{Cl}\cdot$  complex<sup>2</sup> or *t*-BuO $\cdot$  from *t*-BuOCl<sup>3</sup> would have difficulty interpenetrating between the alkane chains and thereby favor terminal chlorination. Any such effect was overshadowed by their high selectivity for secondary over primary hydrogen so that little terminal chlorination took place (Table I).

The general procedure was to reflux RCOOH for 5 hr with a suspension of alumina in  $\text{CCl}_4$ . It was critical to use neutral alumina<sup>4</sup> as the chlorination failed to proceed when basic aluminas were tried. An equimolar amount of  $\text{Cl}_2$  was added and the suspension irradiated with a sun lamp while stirring.

The alumina was separated by filtration and refluxed with acetic acid for 2 days to desorb the products. Thionyl chloride was added to convert both acetic and chloro acids to their acid chlorides. Acetyl chloride was removed by distillation and the remaining acid chlorides converted to methyl esters by addition of methanol. The methyl esters were distilled before analysis.

Analysis by gc was achieved on a Barber-Coleman 5000 instrument using a flame ionization detector, a 6-ft 0.25-in. U column, and a packing of polyethylene-glycol succinate<sup>5</sup> on 100-120 mesh Chromasorb<sup>5</sup> A. Even the methyl 2-8-chlorooctanoates were resolved except for partial overlap of the bands of the 6- and 7-chloro acids. The latter were analyzed using a du Pont 310 curve resolver.

The three methyl chlorobutyrate were identified by observing direct superposition of gc bands with those of authentic samples. Methyl 8-chlorooctanoate was similarly identified. The authentic sample was prepared from cyclooctanone by a procedure identical with that used to prepare methyl 7-chloroheptanoate from cycloheptanone.<sup>6</sup> Strong support for the identification of methyl 8-chlorooctanoate was the observation that its yield dropped sharply in homogeneous chlorination when selective reagents,  $\text{C}_6\text{H}_6\text{Cl}\cdot$  and *t*-BuOCl (Table I), were used.

Methyl 8-chlorooctanoate had the longest retention time as expected. The other chlorooctanoates as well as the chlorohexanoates were provisionally identified on the basis that increasing separation of the chloro and ester groups would lead to increased retention times as was found in the chlorobutyrate.

The products were >90% desorbed by the acetic acid treatment. However, to ensure that the results were not an artifact of selective desorption, a mixture of chlorooctanoic acids from homogeneous chlorination was added to the alumina (5% chloro acid) and de-

(2) G. A. Russell, A. Ito, and D. G. Hendry, *J. Amer. Chem. Soc.*, **85**, 2976 (1963); G. A. Russell, *ibid.*, **80**, 4987, 4997, 5002 (1958); **79**, 2977 (1957).

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(5) Applied Science Laboratories, State College, Pa.

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(1) J. T. Davies and E. K. Rideal, "Interfacial Phenomena," 2nd ed, Academic Press, New York, N. Y., 1963, Chapter 5.