

TABLE II  
VALUES OF THE RATIO  $\Delta F_i / [(\Delta F_H)_1 + (\Delta F_H)_2]^{a,b}$

	<i>i</i>	Cu	Ni	Co
2-Pipecolylamine	1	0.62	0.40	0.31
	2	.51	.32	.25
	3		.19	
2-(2-Aminoethyl)-piperidine	1	.47	.29	
	2	.32	.24	

<sup>a</sup> *t* = 30°; ionic strength  $\rightarrow$  0. <sup>b</sup> Equivalent data for similar ligands are given in ref. 4.

**Interpretations.**—The relative stability of different coordination compounds per unit of base strength for the ligand is shown in Table II. Goldberg and Ferneli<sup>4</sup> in an attempt to estimate the  $\pi$ -bonding contribution to the over-all stability, compared the ratio  $\Delta F / [(\Delta F_H)_1 + (\Delta F_H)_2]$  for ligands which could form  $\pi$ -bonds to the ratio for ligands which could not. Systems

were chosen to minimize other differences in ligands. Steric effects were not too dissimilar and base strength was taken into account in the analysis. This investigation yields data by which 2-picolyamine can be compared to a ligand with closer (though still not identical) steric properties. This comparison shows slightly lower to equal ratios for 2-pipecolylamine compared to ethylenediamine and 2-(2-aminoethyl)-piperidine compared to 1,3-propanediamine, and indicates that the  $\pi$ -bonding contribution of 2-picolyamine and 2-(2-aminoethyl)-pyridine is at least as great as originally supposed.<sup>4</sup>

**Acknowledgment.**—The authors are indebted to the Research Corporation for a Frederick Gardner Cottrell research grant in support of this work, and to Dr. W. C. Ferneli<sup>4</sup> for his many suggestions.

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## Partial Resolution of Some Copper(II) and Nickel(II) $\beta$ -Ketoimine Compounds by Means of a Chromatographic Technique

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Received November 19, 1962

Adsorption of some copper(II) and nickel(II)  $\beta$ -ketoimines on a column of D-lactose, followed by elution with benzene-petroleum ether, effects partial resolution of the compounds into optically active fractions. In all systems, complete recovery of solute was characteristic. The optically active fractions were subject to racemization at rates inversely related to the degree of steric hindrance present in the  $\beta$ -ketoimine. Negative results were obtained in attempts to resolve bis-(4-iminopentane-2-ono)-copper(II) although attempts to resolve the analogous nickel(II) compound were partially successful.

In connection with studies of the kinetics and mechanisms of chelate- and amine-exchange reactions involving  $\beta$ -ketoimine-metal compounds, it was of interest to obtain optically active samples of these compounds. The successful partial resolution of certain trivalent metal acetylacetonates by means of a chromatographic technique using D-lactose<sup>1-3</sup> suggested a possible application to bivalent metal derivatives of  $\beta$ -ketoimines. The existence of enantiomers of the type  $M[R\text{COCHC}(=\text{NR}'')R']_2$  was expected to arise from one of several possible causes: distortion from a planar configuration because of steric interaction of the terminal groups (R, R', and R''), the existence of a tetrahedral configuration, or the existence of an octahedral configuration due to association either with other complex molecules or with solvent.

A few chelating agents capable of forcing a tetrahedral disposition of metal valences have been devised. The most successful of these are 2,2'-bis-(salicylidene-amine)-6,6'-dimethyldiphenyl and 2,2'-bis-(salicylidene-

amino)-diphenyl for which the copper(II), but not the nickel(II), derivatives have been prepared.<sup>4</sup> The resolution of the copper(II) derivatives by a chromatographic technique was suggested, but the results seem never to have been reported.

The third possible cause of optical activity might be expected for nickel(II) compounds. Most nickel chelate compounds suspected of being examples of tetrahedral compounds have been shown to have an octahedral disposition of nickel-donor atom bonds either as a result of inclusion of other ligands within the coordination sphere<sup>5</sup> or as a result of molecular association.<sup>6</sup> It is interesting to note that Craig and Mellor<sup>7</sup> have suggested that tetracoordinate nickel(II) chelate compounds involving O and N donor atoms have a planar distribution of metal valences. Recent studies<sup>8,9</sup> of nickel-salicylaldehyde compounds confirmed the

(4) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **79**, 1273 (1957).

(5) Cf.  $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{N}(\text{NCS})_2]$ : S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

(6) Cf.  $\text{Ni}(\text{R}\text{COCHCOR}')_2$ : G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961); J. P. Fackler, Jr., and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 3775 (1961).

(7) D. P. Craig and D. P. Mellor, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 474 (1940).

(8) J. Ferguson, *J. Chem. Phys.*, **34**, 611 (1960).

(9) R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

(1) T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, **5**, 245 (1958).

(2) T. Moeller, E. Gulyas, and R. H. Marshall, *ibid.*, **9**, 82 (1959).

(3) J. P. Collman and R. P. Blair, Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1961, pp. 5-10.

TABLE I  
 PROPERTIES OF COPPER(II) AND NICKEL(II) COMPOUNDS OF THE TYPE  $[R\text{COCHC}(=\text{NR}')\text{R}'']_2\text{M}$ 

	R	R'	R''	Color	M.p., °C.	Analyses					
						C		H		N	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
Copper(II) chelate compounds											
I	CH <sub>3</sub>	CH <sub>3</sub>	H	Dark gray	185-186	46.23	45.76	6.20	6.33	10.78	10.33
II	CH <sub>3</sub>	CH <sub>3</sub>	2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Green	135	66.71	66.79	6.89	6.76	6.00	6.05
III	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	Light green	178-180	71.70	71.28	5.26	5.33	5.23	5.25
IV	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> <sup>14</sup>	Yellow-green	254-255	76.40	76.50	4.89	5.07	4.24	4.35
Nickel(II) chelate compounds											
V	CH <sub>3</sub>	CH <sub>3</sub>	H	Dark red	247-248	47.10	46.97	6.28	6.43	11.00	11.15
VI	CH <sub>3</sub>	CH <sub>3</sub>	2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Green	219-220	67.40	67.18	6.96	7.06	6.05	6.26
VII	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	Light green	215-216	72.41	72.38	5.33	5.71	5.28	5.22
VIII	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Yellow-green	278-279	76.97	75.99	4.90	4.82	4.30	4.32

validity of this suggestion. However, in a recent communication,<sup>10</sup> the paramagnetism of  $\alpha$ -branched bis-(N-alkylsalicylaldehyde)-nickel(II) compounds in xylene solution is attributed to a conformational equilibrium for which the amount of tetrahedral species increases with temperature.

### Experimental

**Materials.**—As previously outlined,<sup>1,2</sup> freshly opened Baker Analyzed Reagent grade D-lactose hydrate, screened to 100 mesh, was used without further purification. This material was dehydrated by heating at 125-130° for 3 hr. Benzene and low-boiling petroleum ether (30-60°) were dried over sodium wire and anhydrous magnesium sulfate, respectively.

**Preparation of Copper(II) and Nickel(II) Chelate Compounds (Table I).**—All of the  $\beta$ -ketoimines used here were prepared as previously described,<sup>11,12</sup> except 4-iminopentane-2-one, which was purchased from Aldrich Chemical Co.

**Bis-(4-iminopentane-2-ono)-copper(II).**<sup>13</sup>—A solution of 2 g. of 4-iminopentane-2-one in 20 ml. of 95% ethanol was added to 30 ml. of ammoniacal cupric nitrate solution (containing 2.4 g. of cupric nitrate 3-hydrate and 50 drops of 15 M aqueous ammonia). The dark gray needles which immediately formed were allowed to stand overnight, filtered off, and recrystallized from 95% ethanol.

**Bis-[4-(2,6-dimethylphenylimino)-pentane-2-ono]-copper(II).**—This compound was prepared by the addition of ligand (95% ethanol) solution to bis-(4-iminopentane-2-ono)-copper(II) dissolved in ethanol. The mixture was heated on a steam bath. The solution color changed to green, indicating chelate exchange, and a green precipitate gradually formed. It was recrystallized from 95% ethanol.

**Bis-(3-phenylimino-1-phenylbutane-1-ono)-copper(II).**—This compound was obtained by following the procedure described by Struss.<sup>14</sup>

**Bis-(4-iminopentane-2-ono)-nickel(II).**—To a solution containing 0.01 mole of nickel acetate, 50 drops of 15 M aqueous ammonia, and 30 ml. of water, 0.022 mole of 4-iminopentane-2-one in 20 ml. of 95% ethanol was added. The dark red complex was precipitated slowly from solution by heating the mixture on a steam bath. Recrystallization was accomplished using 95% ethanol, and the compound was dried *in vacuo*.

**Bis-[4-(2,6-dimethylphenylimino)-pentane-2-ono]-nickel(II).**

(10) L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962).

(11) D. F. Martin, G. A. Janusonis, and B. B. Martin, *J. Am. Chem. Soc.*, **83**, 73 (1961).

(12) D. F. Martin, in "Reactions of Coordinated Ligands and Homogeneous Catalysis," *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963, pp. 192-200.

(13) H. F. Holtzclaw, Jr., J. P. Collman, and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).

(14) A. W. Struss, B.S. Thesis, University of Illinois, 1962.

—This compound was prepared by chelate exchange similar to that used for the copper(II) chelate but with a slight modification. The quantity of ligand used was twice the theoretically required amount, and the reaction proceeded relatively slowly. A solution of 1 g. of 4-(2,6-dimethylphenylimino)-pentane-2-one in 20 ml. of absolute alcohol was gently heated on a steam bath. To this was added gradually 0.3 g. of solid bis-(4-iminopentane-2-ono)-nickel(II) with stirring to enhance dissolution. The color of the solution changed to light green, and the reaction was allowed to proceed to completion over a period of 3 hr. The solution was cooled in ice-water, and the product was collected and recrystallized from hot 95% ethanol as green crystals.

**Bis-(3-phenylimino-1-phenylbutane-1-ono)-nickel(II).**—A 1.1-g. sample of 3-phenylimino-1-phenylbutane-1-one was dissolved in 20 ml. of absolute alcohol and heated gently on a water bath. To this was added gradually with stirring 0.3 g. of bis-(4-iminopentane-2-ono)-nickel(II) (100% excess of ligand). The color changed from red to dark red. Heating was continued for 3 hr. The solution was cooled in an ice bath with consequent precipitation of excess ligand. The solution was filtered, and upon prolonged cooling a light green precipitate formed. This is the desired product. This precipitate was recrystallized from benzene since the compound is only slightly soluble in alcohol.

**Bis-(1-phenylimino-1,3-diphenylpropane-3-ono)-nickel(II).**—A solution of 0.5 g. of bis-(4-iminopentane-2-ono)-nickel(II) in 20 ml. of absolute alcohol was heated gently on a steam bath. To this was gradually added 1.4 g. of 1-phenylimino-1,3-diphenylpropane-3-one, which was dissolved in 15 ml. of absolute alcohol. The solution was filtered, and the precipitate was washed several times with hot benzene. The product was only slightly soluble in benzene and alcohol. Attempts to purify the compound further were not successful.

**Resolution Procedure.**—A 200-cm. column of 2.5-cm. diameter, equipped with a Teflon stopcock and filled with a 180-cm. length of D-lactose, was used for the chromatographic resolution. A benzene-petroleum ether (1:1) mixture was used as eluent in all experiments. The general procedure was the same as previously described.<sup>1,2</sup> Breakthrough of solute was recognized by the color of the chelate itself. All optical measurements were made at 5983 Å. with a Schmidt and Haensch polarimeter (No. 9143) calibrated to 0.001°. Readings were reproducible to  $\pm 0.003^\circ$ . An average of ten readings was used for each sample, and blank readings were made before and after each sample was observed. Readings on solvent which had passed through the column before the latter was treated with the chelates were identical with the blanks. The quantity of chelate eluted was determined for each sample with a Cary recording spectrophotometer (Model 14M, Serial 83). Racemization was followed at 23-25° by periodic polarimeter readings, using a 101-mm. Pyrex cell.

### Discussion

Typical chromatographic data for the absorption and elution of bis-( $\beta$ -ketoimino)-copper(II) and -nickel-

TABLE II  
 CHROMATOGRAPHIC DATA FOR ADSORPTION AND ELUTION OF COPPER(II) AND NICKEL(II) COMPOUNDS

Com- pound	Solute adsorbed, g.	Chromatographic conditions	Active eluted fractions			
			Quantity recovered, g. <sup>a</sup>	Specific rotation [ $\alpha$ ] <sub>5893</sub>	Max. mol. rotation [M] <sub>5893</sub> <sup>b</sup>	Racemization constant K, hr. <sup>-1</sup>
I	0.0774	Column: 8 drops/min. Breakthrough: 15.4 hr. Total time: 22.5 hr.	0.0756	...	...	...
II	.0460	Column: 10 drops/min. Breakthrough: 11.2 hr. Total time: 17.8 hr.	.0430	+38.41 -33.18	+179.79 -155.31	0.921
III	.0640	Column: 12 drops/min. Breakthrough: 14.7 hr. Total time: 21.5 hr.	.0642	+44.74 -31.79	+239.63 -170.27	.684
IV	.0780	Column: 8 drops/min. Breakthrough: 13.3 hr. Total time: 20.8 hr.	.0768	+50.97 -62.15	+336.40 -410.19	.391
V	.0592	Column: 12 drops/min. Breakthrough: 17 hr. Total time: 21.7 hr.	.0585	+21.24 -23.82	+54.54 -61.18	1.059
VI	.0655	Column: 12 drops/min. Breakthrough: 14.5 hr. Total time: 18.5 hr.	.0625	+39.74 -38.81	+184.08 -179.77	0.402
VII	.0483	Column: 12 drops/min. Breakthrough: 13 hr. Total time: 18 hr.	.0475	+51.39 -45.18	+272.76 -240.80	.222
VIII	.0530	Column: 12 drops/min. Breakthrough: 11 hr. Total time: 18.5 hr.	.0521	+69.70 -53.61	+456.81 -351.36	.125

<sup>a</sup> Determined spectrophotometrically. <sup>b</sup>  $[M]_{5893} = [\alpha]_{5893} \times \text{molecular weight} \times 10^{-2}$ .

(II) compounds are assembled in Table II. In general, the data indicate that at least partial resolution was effected. Bis-(4-iminopentane-2-ono)-copper(II) is exceptional in that it either is not subject to resolution or, if capable of resolution, undergoes racemization at a very high rate. In each case, the levorotatory form of either the copper(II) or nickel(II) compound was the more strongly adsorbed by D-lactose, and it was removed from the column after the dextrorotatory form had been eluted. Elution of the compounds from the adsorbent was quantitative.

The magnitude of the maximum molecular rotation obtained was dependent upon the compound. The values obtained for compound VIII (+456.81°; -351.36°) compare favorably with the value of -570.00° obtained for cobalt(III) acetylacetonate. However, the favorable values may be due to use of a longer column. A 200-cm. column was used in the present study as compared with a 90-cm. column used by previous workers.<sup>1</sup> Collman and Blair<sup>3</sup> reported that the use of a 16-ft. column of D-lactose hydrate afforded *l*-cobalt(III) acetylacetonate with molecular rotations as high as -4450.00°.

The optically active fractions were observed to undergo racemization although no change in the optical rotation of 1:1 petroleum ether-benzene solvent was observed. Moreover the variation of log [ $\alpha$ ] with time was linear in accordance with first-order kinetics. The specific rate constant decreases with increasing number of phenyl or substituted phenyl groups present.

The optical stability of the various fractions compares favorably with other complexes of tetracoördinate metal ions. For example, the maximum specific rate

constant 1.059 hr.<sup>-1</sup> that was observed for bis-(4-iminopentane-2-ono)-nickel(II) is much lower than that calculated for dimethylammonium bis-(benzoylpyruvato)-beryllate.<sup>15</sup>

At this point, it is of interest to speculate on the origin of the optical activity of the bis-( $\beta$ -ketoimino)-copper(II) and -nickel(II) compounds. The suggestion that the presence of terminal groups introduces a distortion from a planar configuration appears to be reasonable for the copper(II) compounds but not for bis-(4-iminopentane-2-ono)-nickel(II). This compound has been partially resolved even though the amount of steric hindrance present is surely slight. The supposition that the structure of the copper(II) complexes is that of a distorted plane formed from a grossly distorted tetrahedron has some support in the similarity between the absorption spectra of the copper(II) complexes and that of the tetrachlorocuprate(II) ion, the structure of which is known to be a grossly distorted tetrahedron.<sup>16</sup> The spectra of the copper(II) chelate compounds (Table III) show intense absorption in the region 285-300 m $\mu$  as compared with an intense absorption band at 308 m $\mu$ <sup>16</sup> for the tetrachlorocuprate(II) ion (solid state).

A second possible explanation of the optical activity is that it arises from some asymmetric hexacoördinate species. This type of species might be expected, especially for the nickel(II) compounds, although several examples of hexacoördinate copper(II)<sup>17</sup> are known. It is possible to envision a polymeric structure that is

(15) *Ca.* 10 hr.<sup>-1</sup> at 20° in alcohol: W. H. Mills and R. A. Gotts, *J. Chem. Soc.*, 3121 (1926).

(16) L. Helmholtz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

(17) P. G. Owston, *Ann. Rept.*, **58**, 465 (1961).

TABLE III  
ULTRAVIOLET ABSORPTION SPECTRA OF BIS-( $\beta$ -KETOIMINO)-  
COPPER(II) AND -NICKEL(II) COMPOUNDS<sup>a</sup>

Copper(II) chelate compounds			Nickel(II) chelate compounds		
Com- pound	Max., m $\mu$	$\epsilon \times 10^{-4}$ , l. mole <sup>-1</sup> cm. <sup>-1</sup>	Com- pound	Max., m $\mu$	$\epsilon \times 10^{-4}$ , l. mole <sup>-1</sup> cm. <sup>-1</sup>
I	278	...	V	298	0.415
	302	1.60		348	0.476
	360	0.155		364	0.446
II	285	2.40	VI	274	3.00
	312	2.00		363	0.458
III	292	2.30		VII	382
	354	3.20	277		0.802
IV	297	2.40	VIII	350	2.08
	375	3.75		277	1.72
				377	4.15

<sup>a</sup> Solvent: 1:1 benzene-petroleum ether (b.p. 30-60°).

analogous to that observed for nickel(II) acetetylacetonate,<sup>8</sup> and structures involving hexacoordinate nickel have been observed for salicylaldimine compounds.<sup>18</sup> It is also possible that copper(II) could achieve a hexacoordinate structure through metal-metal bonding. However, two observations suggest that the optical activity is not due to a hexacoordinate species. In the first place, the compounds for which the optical activity and stability are the greatest, *i.e.*, compounds IV and VIII, are the least likely to achieve a hexacoordinate structure because of steric hindrance. Moreover, molecular weight data from benzene solutions indicate that the nickel(II) and copper(II) compounds exist as monomers.<sup>19</sup>

A third possible explanation is that optical activity is a consequence of the existence of a tetrahedral species which may be slightly distorted. This explanation appears to be applicable to bis-(4-iminopentane-2-ono)-nickel(II) and possibly to the other nickel(II) compounds. The behavior of the former cannot be explained by the existence of a planar or hexacoordinate configuration. The latter compounds may have a tetrahedral structure. This is suggested by the observation that the optical stability of the nickel(II) compounds is much greater than that of the copper(II) analogs.

(18) Cf. R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).

(19) Molecular-weight data (compound: calculated, found): IV: 660, 580; V: 255, 247; VI: 463, 435; VIII: 531, 441. These data were obtained by Mr. J. Nemeth.

The mechanism of the loss of optical activity of the copper(II) and nickel(II) chelate compounds is not known, but some pertinent observations can be made. The mechanism could involve an intermolecular or an intramolecular process. The latter mechanism might be favored on the grounds that the transformation from a distorted plane to a planar intermediate would require less energy than dissociation. Further, there is a precedent for this transformation in the square planar-tetrahedral isomerism observed for certain nickel(II) complexes.<sup>20</sup> The intermolecular process might be favored in view of the observed lability of many copper(II) and nickel(II) compounds.

In a preliminary effort to elucidate the mechanism of racemization, the effect of added ligands on the rate of racemization was studied. The specific rate constant for the racemization of compound VII is 0.125 hr.<sup>-1</sup>, and, in the presence of a large excess of 1-phenylimino-1,3-diphenylpropane-3-one (ligand:complex molar ratio = 7.6:1), the specific rate constant was 4.2 hr.<sup>-1</sup>. Similarly, the specific rate constant for the loss of optical activity was 0.43 hr.<sup>-1</sup> when aniline (aniline: complex molar ratio = 7.3:1) was present. These data are in accord with the view that the racemization is an intermolecular process. An alternate view is that the rate constants obtained when an excess of  $\beta$ -ketoimine or aniline was present are actually a measure of the rate of chelate exchange and amine exchange, respectively. This seems unlikely because the rate constant is substantially greater than would have been expected on the basis of preliminary studies of the rate of amine exchange,<sup>21</sup> because, in general,  $\beta$ -ketoimine-nickel(II) compounds do not undergo chelate exchange.<sup>14</sup> The fact that a much greater specific rate constant was obtained when an excess of  $\beta$ -ketoimine was present is more nearly consistent with an intermolecular process. Thus, although a definite statement concerning the mechanism of racemization must await studies of the rate of exchange, present evidence favors the intermolecular process.

**Acknowledgment.**—We wish to express our gratitude for the support of this investigation by PHS Research Grant 7873, Division of General Medical Sciences, U. S. Public Health Service.

(20) R. G. Hayter and F. S. Humiec, *J. Am. Chem. Soc.*, **84**, 2004 (1962).

(21) E. J. Olszewski, private communication.