

# A NEW SOURCE OF OPTICAL ACTIVITY IN COORDINATION CHEMISTRY

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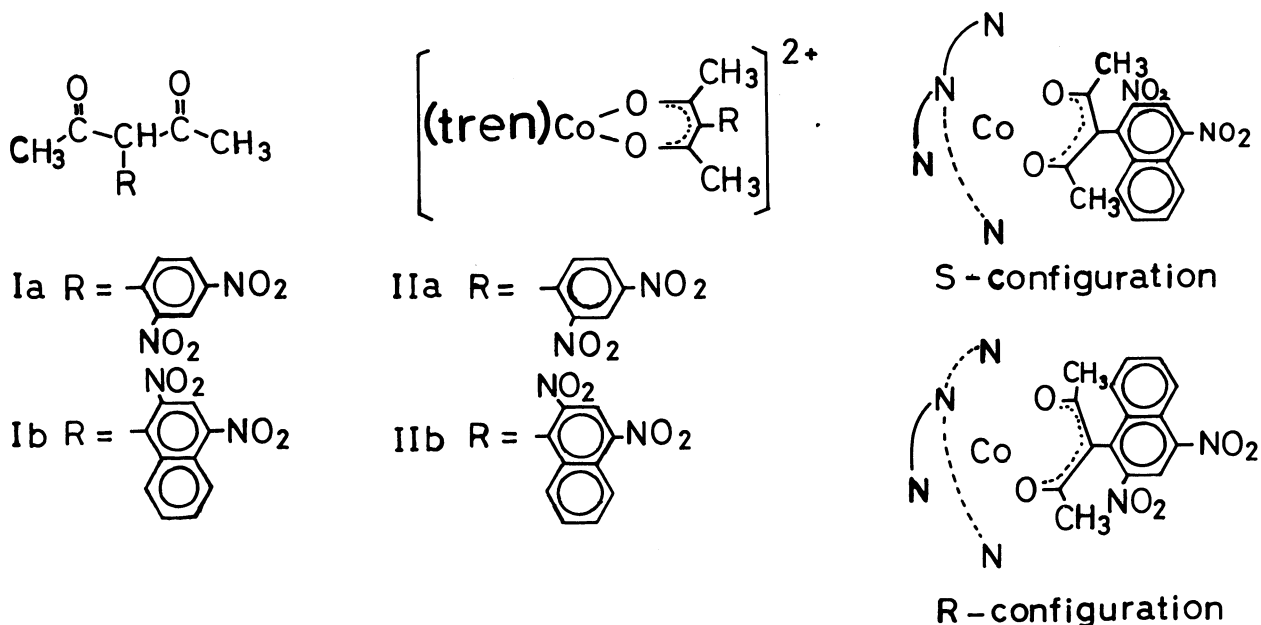
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An optically active complex of which chirality is due to restricted rotation of a remote group was prepared and resolved.

In coordination compounds were found various sources of optical activity. Both empirical and theoretical methods had been proposed to relate CD spectral properties to absolute configuration, but with no final success.<sup>1)</sup> A new source of optical activity is reported in this letter, and we hope that it can help to clarify the phenomena of optical activity.

In complex IIb unsymmetric aromatic ring is perpendicular to  $\beta$ -diketonate ring, and cannot rotate due to steric hindrance. Optical activity occurs from relative configuration between the substituted aromatic ring and 2,2',2'',-tri-aminotriethylamine(tren).

Reaction of sodium acetylacetonate with the 2,4-dinitro-chloro substituted derivatives gave ligands Ia and Ib. Procedures used for the preparation of IIa and IIb are modification of Reid and Sargeson.<sup>2)</sup>



An aqueous solution of  $[\text{Co}(\text{CO}_2\text{tren})^+]$  <sup>3)</sup> was acidified (pH 1.5) and stirred for half an hour. The solution was brought to pH 8.5 and Ia or Ib was added. The reaction mixture was heated to 60°C under stirring. In the case of complex IIa, addition of excess sodium perchlorate or potassium iodide to the reaction mixture directly resulted in precipitation of the complex IIa. But cation exchange chromatography by SP-sephadex with 0.5 mole/l sodium chloride as eluant was necessary to isolate IIb. When sodium bromide was added to the eluate, bromide of IIb precipitated. Yield of IIb: 60%      Analytical data of IIb. Found; C, 37.06; H, 4.32; N, 12.38%. Calcd for  $\text{CoC}_2\text{H}_2\text{N}_6\text{Br}_2$ : C, 37.08; H, 4.30; N, 12.36%.

Infra-red spectra of IIa and IIb did not show clear characteristic peaks of substituted  $\beta$ -diketonate ring due to strong absorption of two nitro groups. Chloride of IIb which was obtained from bromide of IIb by means of anion exchange chromatography was suitable for a sample of PMR measurement. The spectrum of IIb was as follows; 7.82 and 7.69 $\tau$  both singlet( $\text{CH}_3$ ), 5.4~4.7 $\tau$  broad peak( $\text{CH}_2$ ), 3.7~4.3 $\tau$  broad( $\text{NH}_2$ ), 0.8~1.9 $\tau$  multiplet(aromatic protons).

Complex IIb was resolved, but IIa was not. Cation exchange chromatography by SP-sephadex was repeated with 0.2 mole/l antimonyl potassium tartrate as eluant. The active complex was eluted as two completely separate bands, an fraction of (-)-complex was faster than that of (+)-complex. Optical rotations were measured with automatic polarimeter model DIP-180 of Japan Spectroscopic Co. Ltd; (-)-complex  $[\text{M}]_D^{20} = -1250$  and (+)-complex  $[\text{M}]_D^{20} = +1280$ .

Unsymmetric aromatic ring would slip to enantiomer in the case of complex IIa.

#### References

- 1) C.J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience (1972).
- 2) I.K. Reid and A.M. Sargeson, "Inorganic Syntheses", Vol.IX, p.167(1967).
- 3) E. Kimura, S. Young, and J.P. Collman, Inorg. Chem., 9, 1183(1970).

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