Short Communications

Cotton Effects of *d-d*-Transitions of Optically Active Nickel(II)-Thiosemicarbazide Complexes

K. A. JENSEN, S. BURMESTER, G. CEDERBERG, R. B. JENSEN and C. TH. PEDERSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

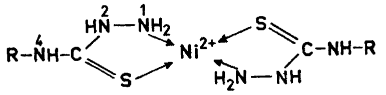
and

ERIK LARSEN

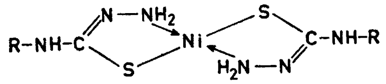
Chemical Laboratory I (Inorganic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

Hawkins[1] has recently presented the first definite example of Cotton effects in *d-d*-transitions of metal complexes induced by a chelate group containing an asymmetric carbon atom outside the metalchelate ring atoms. The ligand used was (−)-N,N′-bis(1-(chloromethyl)propyl)ethylenediamine which forms optically active copper(II) complexes of unknown structure. The effect was very small.

In this paper it is shown that nickel(II) complexes of optically active thiosemicarbazides (prepared from optically active



I



II

amines) of the general type I or II may exhibit circular dichroism.

R is a carbon radical containing an asymmetric carbon atom. The structure of such complexes is well known[2-4] and the Cotton effects observed are appreciable. Therefore, a study of the circular dichroism of these complexes has considerable stereochemical interest.

The absorption and circular dichroism spectra have been measured in ethanolic solutions of the ionic complexes, I (as chlorides). Due to their low solubility, the inner complexes II could not be studied quantitatively, and the following discussion therefore only refers to the ionic type of complexes.

The results given in Table 1 show that the complexes containing the bulky 3(*R*)-menthyl- and (*S*)-α-methylbenzyl groups have higher circular dichroism intensities than those containing the (*R*)-*sec*-butyl group. Further, the intensity of the circular dichroism is higher for the 2-methyl substituted thiosemicarbazide complexes. The sign of the observed circular dichroism in the *d-d*-transitions is positive for the complexes derived from thiosemicarbazides of *R* configuration and negative for those of *S* configuration.

It has been found that only when the α-carbon in the R group is asymmetric a Cotton effect is observed. Thus, no circular dichroism was observed when the radical in the 4-position was (*S*)-(2-methyl)butyl.

According to the present theories of optical activity in metal complexes, a necessary condition for the chromophore to exhibit optical activity is that the two chelate rings in the complex have the same out-of-plane conformation. The asymmetric carbon atoms may exert, through the N^4 atoms, a continuous asymmetric transformation on the chelate rings by forcing them to occupy such out-of-plane conformations. The N^4 atom will also become asymmetric (although this is not

Table 1 *

Nickel complex of:	Dichrogram		Absorption spectrum	
	λ_{max}	$\Delta\varepsilon_{max} \times 10^{-2}$	λ_{max}	ε
R^1-NH-CS-NH-NH_2	435 570	−26.5 −8.5	435	49.3
R^1-NH-CS-N(CH_3)-NH_2	423 565	−120 −32	428	128
R^1-NH-CS-N(CH_3)-$NHCH_3$	440	−16	440	47
R^2-NH-CS-NH-NH_2	500	10.0	440 480	84 79
R^2-NH-CS-N(CH_3)-NH_2	490 555	25 23	438	130
R^4-NH-CS-NH-NH_2	440 575	−2.5 −2.5	440	32.1
R^4-NH-CS-N(CH_3)-NH_2	425 560	−7.5 −37.5	431	107

* No circular dichroism was observed with the thiosemicarbazides R^1-NH-CS-NH-N(CH_3)$_2$ and R^1-NH-CS-NH-NHC_6H_5, which do not form nickel complexes of type I, and with R^3-NH-CS-NH-NH_2 and R^3-NH-CS-N(CH_3)-NH_2, in which the α-carbon in the R group is not asymmetric.

considered essential). It is thought that amine radicals having bulky groups around the nearest asymmetric carbon atom might produce equilibria favouring one of the configurations of the chelate rings more than the other. According to the general rules for asymmetric synthesis the conformation of the chelate ring, and thus the sign of the circular dichroism, will be correlated with the configuration of the asymmetric carbon atom.[5,6] However, the observed circular dichroism magnitudes are surprisingly large to be explained by the effect of an asymmetric transformation over several atoms and thus suggests a more effective interaction between the asymmetric carbon atom and the metal chelate ring than the normal dispersion forces. A probable explanation seems to be that the conformation of the chelate ring is stabilised by hydrogen bonds from N^2 and N^4 to a common solvent molecule.

If the stability of the configuration of the chelate ring is determined by the "asymmetric bulkyness" of the amine it is expected that the sign of the circular dichroism of the corresponding nickel(II) thiosemicarbazide complexes generally will reflect the absolute configuration of the amine.

Experimental. Circular dichroism measurements were performed with a Roussel-Jouan Dichrograph. The absorption spectra were measured with a Cary Model 14 recording spectrophotometer, and the optical rotations with a Perkin-Elmer polarimeter 149.

The optically active amines were prepared as described in the literature.[8-11] It proved necessary to work with amines of high optical purity. Thus, 4-*sec*-butylthiosemicarbazide prepared from (+)-*sec*-butylamine with an optical purity of 28 % became almost inactive on recrystallisation because the racemic compound had the lowest solubility.

Thiosemicarbazide	m.p., °C	Formula	Analyses (C, H, N)	g in 100 ml of abs. ethanol	$[\varphi]\lambda^{25}$ λ (mμ) 313	364	436	546	578	589
R^1-NH-CS-NH-NH_2	75—76	$C_9H_{13}N_3S$		0.5891	−554°	−447°	−208°	−94.5°	−80.1°	−81.6°
R^1-NH-CS-N(CH_3)-NH_2	105—106	$C_{10}H_{15}N_3S$	Calc.: 57.42; 7.18; 20.01 Found: 57.30; 7.08; 19.83	0.8063	−295°	−277°	−126.3°	−56.2°	−47.9°	−48.7°
R^1-NH-CS-N(CH_3)-$NHCH_3$	68.5—69.5	$C_{11}H_{17}N_3S$	Calc.: 59.15; 7.61; 18.84 Found: 59,20; 7,68; 18,60	0.6931	−177.4°	−181.4°	−65.2°	−20.3°	−16.4°	−16.1°
R^1-NH-CS-NH-N$(CH_3)_2$	144—145	$C_{11}H_{17}N_3S$	Calc.: 59.15; 7.61; 18.84 Found: 59.10; 7.81; 18.92	0.7578	−358°	−326°	−127.3°	−48.8°	−38.8°	−38.8°
R^1-NH-CS-NH-NHC_6H_5	158—159	$C_{15}H_{17}N_3S$	Calc.: 66.42; 6.27; 15.50 Found: 66.10; 6.57; 15.31	0.6423	355°	366°	247°	128.6°	113.8°	115.3°
R^2-NH-CS-NH-NH_2	172—174	$C_{11}H_{23}N_3S$	Calc.: 57.60; 10.04; 19.20 Found: 57.45; 9.94; 18.31	0.2277		−733°	−471°	−274°	−240°	−246°
R^2-NH-CS-N(CH_3)-NH_2	178—179	$C_{12}H_{25}N_3S$	Calc.: 59.26; 10.29; 17.28 Found: 59.10; 10.08; 17.38	0.9113	−1049°	−637°	−569°	−329°	−262°	−295°
R^3-NH-CS-NH-NH_2	69.5—70.5	$C_6H_{15}N_3S$	Calc.: 44.72; 9.32; 26.09 Found: 44.64; 9.33; 25.75	0.4297	37.0°	37.1°	18.7°	10.1°	9.7°	9.7°
R^3-NH-CS-N(CH_3)-NH_2	73—74	$C_7H_{17}N_3S$	Calc.: 48.00; 9.71; 24.00 Found: 47.90; 9.57; 23.96	0.4216		37.3°	24.1°	17.0°	14.1°	14.5°
R_4-NH-CS-NH-NH_2	55—56	$C_5H_{13}N_3S$	Calc.: 40.80; 8.90; 28.55 Found: 40.91; 8.91; 28.37	1.517		65.9°	48.9°	31.2°	28.7°	28.2°
R_4-NH-CS-N(CH_3)-NH_2	84—86	$C_6H_{15}N_3S$	Calc.: 44.70; 9.38; 26.07 Found: 44.72; 9.26: 25.83	1.290		86.1°	60.1°	36.9°	33.2°	33.4°

* In the Tables R^1, R^2, R^3, and R^4 have the following meaning:
R^1 = (*S*)-α-Methylbenzyl
R^2 = 3(*R*)-Menthyl
R^3 = (*S*)-2-Methylbutyl
R^4 = (*S*)-*sec*-Butyl

The optically active amines were transformed into optically active isothiocyanates as described in the literature [8,12,13] except that (*R*)-menthylisothiocyanate was prepared by the thiophosgen method.

The thiosemicarbazides were prepared as described by Jensen *et al.*[14] for the racemic thiosemicarbazides from the optically active isothiocyanates and hydrazine or substituted hydrazines. With the exception of (*S*)-4-α-methylbenzylthiosemicarbazide ((*S*)-4-α-phenethylthiosemicarbazide) which has been described by Ohlsson [13] all the optically active thiosemicarbazides are new. For analyses, *etc.*, see Table 2.

The thiosemicarbazide complexes were prepared from nickel(II) chloride and the thiosemicarbazides in alcoholic solution as described by Jensen and Rancke Madsen.[2] Usually the complexes were not isolated but the alcoholic solutions were used directly for the measurements (see Table 1).

1. Hawkins, C. J. *Acta Chem. Scand.* **18** (1964) 1564.
2. Jensen, K. A. and Rancke Madsen, E. *Z. anorg. allgem. Chem.* **219** (1934) 243; Jensen, K. A. *Z. anorg. allgem. Chem.* **221** (1934) 11; **229** (1936) 265.
3. Grønbæk, R. and Rasmussen, S. E. *Acta Chem. Scand.* **16** (1962) 2325.
4. Cavalca, L., Nardelli, M. and Fava, G. *Acta Cryst.* **15** (1962) 1139; Nardelli, M. and Boldrini, P. *Gazz. Chim. Ital.* **91** (1961) 280.
5. Cram, D. J. and Abd Elhafez, F. A. *J. Am. Chem. Soc.* **74** (1952) 5828.
6. Prelog, V. *Helv. Chim. Acta* **36** (1953) 308.
7. Thomé, L. G. *Ber.* **36** (1903) 582.
8. Kjær, A. and Friis, P. *Acta Chem. Scand.* **16** (1962) 936.
9. Kuthe, M. *Ann.* **276** (1893) 300.
10. Tutin, F. and Kipping, F. S. *J. Chem. Soc.* **85** (1904) 69.
11. Ingersoll, A. W. *Org. Syn.* Coll. Vol. **II** 506.
12. Billetter, O. and Steiner, A. *Ber.* **20** (1887) 228.
13. Ohlson, E. *4-Fenethyltiosemicarbazid, en preparativ, stereokemisk och kinetisk studie, Diss.*, Lund 1917.
14. Jensen, K. A. *et al. Acta Chem. Scand. To be published.*

Received April 26, 1965.

Studies on the Determination of Isothiocyanates and Vinyl-Oxazolidinethione in Seeds of Rape and Turnip Rape

L.-Å. APPELQVIST and E. JOSEFSSON

Chemical Department, Swedish Seed Association, Svalöv, Sweden

As the amount of thioglucosides in seed meals from rape and turnip rape limits their use as animal feed, investigations into the varietal differences in content of the split products from the thioglucosides were initiated.[1,2] It was found, however, that the analytical methods of Wetter [3,4] were not wholly satisfactory, with regard to the precision obtainable. Furthermore a less tedious method was regarded as essential.

The following steps of the procedure of Wetter have been studied and changed, *viz:* the pH of the myrosinase reaction, the separation of isothiocyanates (I) from oxazolidinethiones (II), and the determination of I. Also pretreatments of the seed and the defatted seed meal are included in our method. According to Schwimmer [5] the pH-optimum of the myrosinase reaction is 6–7. Wetter,[3] however, reported the optimum conditions for release of I from rapeseed meal to be at pH 4. This discrepancy prompted us to look for some destructive agents in crude rapeseed meal.

Van Etten *et al.*[6] found higher II content in *Crambe Abyssinica* seed meal, when hot water extracts of thioglucosides were incubated at pH 7, than at pH 4 as in Wetter's method. They estimate, however, volatile I after release at pH 4. As I at pH > 5 reacts with proteins (see, *e.g.*, Edman [7] and Goksöyr [8]), an apparent pH-optimum of 4 for the I release, as reported by Wetter, is easily explained.

André [9] avoided the loss of I in unbuffered reaction systems by treating the meal with hot water, cooling the slurry and adding a myrosinase preparation.

Attempts to extract the thioglucosides by successive hot water aliquots as in the procedure of van Etten *et al.*[6] were found to give higher II values than when the slurry was incubated at pH 4. This is partly due to the slow cyclization of the 2-hydroxy-3-butenylisothiocyanate to vinyloxazolidinethione at acid pH. As the