

5. Evelyn, K. A., Malloy, H. T. und Rosen, C. *J. Biol. Chem.* **126** (1938) 645.
6. Ponting, J. D. *Ind. Eng. Chem. Anal. Ed.* **15** (1943) 389.
7. Loeffler, H. J. und Ponting, J. D. *Ind. Eng. Chem. Anal. Ed.* **14** (1942) 846.
8. Sereno, M. N., Highlands, M. E., Cunningham, C. E. und Getchell, J. S. *Maine Agr. Expt. Sta. Bull. No.* **563** (1957).
9. Jaarma, M. *Arkiv Kemi* **13** (1958) 97.
10. Schwimmer, S., Burr, H. K., Harrington, W. O. und Weston, W. J. *Am. Potato J.* **34** (1957) 31.

Eingegangen am 21. Januar 1963.

## Adducts of Nickel(II) Diethyldi- thiophosphate with Secondary Ami- nes and Heterocyclic Diimines

CHR. KLIXBÜLL JØRGENSEN,

*Cyanamid European Research Institute,  
Cologny (Geneva), Switzerland*

The low-spin purple compound  $\text{Ni dtp}_2 = \text{Ni}(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_2$  forms an addition compound with two molecules of pyridine. The resultant high-spin pale green  $\text{Ni dtp}_2\text{py}_2$  was first prepared by W. Conrad Fernelius<sup>1</sup>. Mixed  $\text{dtp}^-$  complexes containing other ligands on the residual places are not well known though ethanol solvates of  $\text{Co dtp}_2$  have been detected<sup>2</sup>. Portions of 0.01 M  $\text{Ni dtp}_2$  solutions in 1,2-dichloroethane were mixed with various amines in the same solvent. Incidentally, these amines form weak charge-transfer complexes with the solvent<sup>3</sup>. In the case of aniline, diphenylamine and acetonitrile, the purple colour was not much changed, whereas ethanolamine, diethanolamine, triethanolamine, ethylenediamine, trimethylenediamine and gaseous ammonia produced very pale blue-greenish colours. In the case of the diamines and  $\text{NH}_3$ , these colours soon turned pale violet, as characteristic of the high-spin complexes, and precipitates of decomposition products occurred after a few hours.

However, most secondary amines gave very strong yellow or orange colours. A characteristic example is di(butyl)amine which is a quite mediocre ligand, as are most other secondary amines, in aqueous

and alcoholic solution for metallic cations. A solution 0.5 M  $(\text{C}_4\text{H}_9)_2\text{NH}$  forms nearly quantitatively the yellow complex with the spectrum given in Table 1. If only 0.1 M  $(\text{C}_4\text{H}_9)_2\text{NH}$  is present at 25°C, about equal amounts of the yellow adduct and of  $\text{Ni dtp}_2$  occur, *i.e.* the formation constant is roughly 10 litre/mole. When the yellow solutions at higher amine concentration are heated, they turn reversibly purplish grey, showing that the complex is formed under evolution of heat. The occurrence of purple-yellow colour shifts in nickel(II) complexes usually correspond to high-spin — low-spin equilibria<sup>4,5</sup>. Yet this is hardly the case here since already the purple, original compound is low-spin. The writer believes that the yellow adduct has a distorted 5-coordination comparable to that of mixed nickel(II) arsine-halides<sup>6,7</sup>. The high intensities, compared to the low intensity of bands<sup>1</sup> of  $\text{Ni dtp}_2\text{py}_2$  is a strong argument against any approximately regular octahedral coordination. The absence of any absorption band in the region between 8000 and 13 000  $\text{cm}^{-1}$  further on indicates low-spin behaviour.

As seen of Table 1, di(isobutyl) amine shows nearly the same behaviour as di(butyl)amine though the yellow colour is slightly less intense. Diethylamine and di(cyclo-hexyl)amine show yellow-brown colours changing to bright yellow with a great excess of amine. Piperidine,  $(\text{CH}_2)_5\text{NH}$ , slowly decomposes the complex, forming first a lemon-yellow colour and then nearly colourless crystals. It is seen of Table 1 that this decomposition is slower in more dilute piperidine, and that the yellow adduct must have a remarkably high formation constant (above 200) since it persists at very low concentrations of free amine. In the brownish violet mixtures with unreacted  $\text{Ni dtp}_2$ , the bands at 685  $\text{m}\mu$  ( $\epsilon = 75$ ) and 523  $\text{m}\mu$  ( $\epsilon = 91$ ) influences the position of the maxima of the actual mixture, and the half-widths increase. Di(benzyl)amine does not form the yellow adduct as readily as the aliphatic secondary amines. Tertiary amines at 1 molar concentration only seem to give some 20 % of the yellow form. This should not be due to impurities of secondary amines since all the amines and diimines used here are Fluka puriss.

There was not found any sign of interaction between  $\text{Ni dtp}_2$  and bromide ions deriving from  $\text{N}(\text{C}_4\text{H}_9)_4^+\text{Br}^-$  such as would have been expected of a square-pyramidal  $\text{NiS}_4\text{Br}$  chromophore<sup>8,12</sup>. Krebs, Weber

Table 1. Absorption bands (shoulders in parentheses) of Ni dtp<sub>2</sub> adducts.

	Wavelength		$\epsilon$	Half-widths cm <sup>-1</sup>
	m $\mu$	cm <sup>-1</sup>		
0.5 M di(butyl)amine	776	12 900	180	$\delta(-) = 1400$
	463	21 600	480	$\delta(-) = 1300$
1 M di(isobutyl)amine	776	12 900	86	$\delta(-) = 1500, \delta(+)= 1600$
	(555)	(18 000)	(35)	
	463	21 600	212	
1 M di(benzyl)amine	706	14 150	56	$\delta(-) = 1700, \delta(+)= 1600$
	(520)	(19 200)	(56)	
	460	21 800	81	
1 M piperidine	740	13 500	36	$\delta(-) = 1500$
	445	22 500	86	
	after 1 hour	720	13 900	
0.2 M piperidine	423	23 600	70	$\delta(-) = 1800$ $\delta(-) = 1500, \delta(+)= 1400$
	752	13 300	66	
	453	22 100	168	
after 1 hour	750	13 300	43	$\delta(-) = 1400$ $\delta(-) = 1400, \delta(+)= 1300$
	451	22 200	101	
	760	13 150	103	
0.04 M piperidine	458	21 800	242	$\delta(-) = 1200$ $\delta(-) = 1550, \delta(+)= 1700$
	746	13 400	90	
	(538)	(18 600)	(54)	
0.008 M piperidine (0.005 M Ni dtp <sub>2</sub> )	459	21 800	184	$\delta(-) = 1300$
	700	14 300	45	
	520	19 200	46	
1 M tri(butyl)amine	(453)	(22 100)	(56)	$\delta(-) = 1300$
	695	14 400	54	
	522	19 100	57	
1 M triethylamine	(453)	(22 100)	(57)	$\delta(-) = 1000$
	1100	9 000	50	
	<sup>1</sup> $\Gamma_3$	(960)	(10 400)	
Ni dtp <sub>2</sub> phen	a <sup>3</sup> $\Gamma_4$	668	15 000	$\delta(-) = 1600, \delta(+)= 1400$
	<sup>3</sup> $\Gamma_5$	1120	8 950	
	<sup>1</sup> $\Gamma_3$	(960)	(10 400)	
Ni dtp <sub>2</sub> dip	a <sup>3</sup> $\Gamma_4$	666	15 000	$\delta(-) = \delta(+)= 1650$

and Fassbender<sup>8</sup> prepared dark-green adducts of dip =  $\alpha, \alpha'$ -dipyridyl with nickel(II) xanthates. Contrary to the case of Ni(S<sub>2</sub>COR)<sub>2</sub>py<sub>2</sub> with the two pyridine molecules in *trans*-position<sup>1</sup>, the two nitrogen atoms of dip and of phen = *o*-phenanthroline are necessarily in *cis*-position. Addition of equimolar amounts of crystalline dip and phen-monohydrate to 0.01 M Ni dtp<sub>2</sub> in dichloroethane resulted in the formation of absinth-green solutions which yielded bright green crystals after evaporation. Table 1 shows that the corresponding absorption spectra belong to high-spin complexes with higher intensity than Ni dtp<sub>2</sub>py<sub>2</sub> but relatively closer to octahedral symmetry, as expected of a *cis*-complex. The value of  $\Delta$  derived from the first absorption band permits an estimate from

the rule of average environment<sup>9</sup> of  $\Delta = 7400$  cm<sup>-1</sup> for the hypothetical complex Ni dtp<sub>3</sub><sup>-</sup> since  $\Delta$  of Ni phen<sub>3</sub><sup>2+</sup> is 12 200 cm<sup>-1</sup>. The former value is 87 % of the value for the hexaaqua ion, whereas the ratio between  $\Delta = 14 400$  cm<sup>-1</sup> of Cr dtp<sub>3</sub> and  $\Delta = 17 400$  cm<sup>-1</sup> of Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> is 83 %. Unfortunately, it is not possible to determine a reliable value for the nephelauxetic ratio  $\beta_{35}$  from the two first spin-allowed transitions in Ni dtp<sub>2</sub>dip and Ni dtp<sub>2</sub>phen. However, the shoulder at 10 400 cm<sup>-1</sup> representing the first spin-forbidden transition indicates a value<sup>10,11</sup> of  $\beta_{33} = 0.61$ , slightly lower than in the bromide-perovskites, which is quite plausible for these relatively covalent Ni(II) complexes.

If only the stoichiometric amount of ethylenediamine = en is added to a 0.01 M

solution of Ni dtp<sub>2</sub> in dichloroethane, some evidence can be found for the existence of high-spin Ni dtp<sub>2</sub>en, since a band at 1100 m $\mu$  ( $\epsilon \approx 18$ ) and a shoulder at 940 m $\mu$  are observed. The subsequent bands at 678 m $\mu$  ( $\epsilon = 38$ ) and 525 m $\mu$  ( $\epsilon = 32$ ) are probably caused, in part, by unreacted Ni dtp<sub>2</sub>.

1. Jørgensen, C. K. *J. Inorg. Nucl. Chem.*
2. Jørgensen, C. K. *Acta Chem. Scand.* **16** (1962) 2017.
3. Stevenson, D. P. and Coppinger, G. M. *J. Am. Chem. Soc.* **84** (1962) 149.
4. Jørgensen, C. K. *Acta Chem. Scand.* **11** (1957) 399.
5. Jørgensen, C. K. *Z. anorg. Chem.* **316** (1962) 12.
6. Harris, C. M., Nyholm, R. S. and Phillips, D. J. *J. Chem. Soc.* **1960** 4379.
7. Barclay, G. A., Nyholm, R. S. and Parish, R. V. *J. Chem. Soc.* **1961** 4433.
8. Krebs, H., Weber, E. F. and Fassbender, H. *Z. anorg. Chem.* **276** (1954) 128.
9. Jørgensen, C. K. *Acta Chem. Scand.* **10** (1956) 887.
10. Jørgensen, C. K. *Advan. Chem. Phys.* **5** (1963) 33.
11. Jørgensen, C. K. *Progr. Inorg. Chem.* **4** (1962) 73.
12. Beck, M. T. and Bjerrum, J. *Acta Chem. Scand.* **16** (1962) 2050.

Received January 9, 1963.

## Studies on the Degradation of Lignin and Model Compounds. I. The Configuration of Dehydrodi-isoeugenol

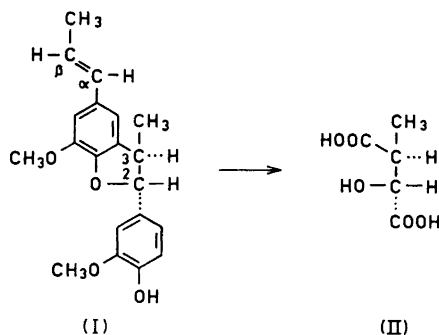
GUNHILD AULIN-ERDTMAN and YUTAKA TOMITA

*Träkemiska Institutionen,*

and (in part) STURE FORSÉN

*Kärnresonansgruppen, Fysikalisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden*

Dehydrodi-isoeugenol (I) was first obtained by Cousin and Hérissé in 1908 through oxidative coupling of isoeugenol<sup>1</sup>. The structure was elucidated by Erdtman in 1933<sup>2</sup> and later confirmed<sup>3-5</sup>. A large



number of studies have since then been carried out on the properties and reactions of dehydrodi-isoeugenol, which is an important lignin model compound. Its configuration, however, has remained unknown, although it is of interest for the understanding of the mechanism of the coupling reaction.

We have now found by IR and PMR investigation that the side-chain of dehydrodi-isoeugenol has the *trans*-configuration. The compound shows a strong IR band at ca. 960 cm<sup>-1</sup>, disappearing on hydrogenation of the side-chain, but no band at 710 cm<sup>-1</sup>. *Trans*-isoeugenol absorbs<sup>6</sup> at ca. 960 cm<sup>-1</sup> and *cis*-isoeugenol<sup>7</sup> at ca. 710 cm<sup>-1</sup>. The PMR spectrum (S. Forsén) of dehydrodi-isoeugenol in carbon tetrachloride solution (internal reference: tetramethyl silane) shows a doublet at  $\delta = 1.83$  ppm, due to the methyl group of the side-chain. The spin coupling constant between the methyl protons and the proton at the  $\beta$ -carbon atom is 5.2 c/s. The coupling constant between the methyl protons and the proton at the  $\alpha$ -carbon atom is less than 0.5 c/s. These values are in excellent agreement with the corresponding values found for *trans*-isoeugenol while for *cis*-isoeugenol the figures are 6.9 and 1.6 c/s, respectively.

We have found that, apparently, *cis*-isoeugenol does not give any dehydrodi-isoeugenol with ferric chloride. Using Leopold's procedure<sup>8</sup>, *trans*-isoeugenol gave a 30% yield of dehydrodi-isoeugenol, which crystallized during the reaction. A mixture of *trans*- and *cis*-isoeugenol (1:1) gave a 15% yield of dehydrodi-isoeugenol while *cis*-isoeugenol gave a non-crystalline product.

The configuration of the coumarane portion of dehydrodi-isoeugenol was determined by treating the compound with