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Note

New Mixed Ligand Complexes of Ditertiary Phosphanes with Ni(II) Alkylxanthates

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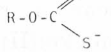
Mixed ligand complexes of Ni(II) with alkylxanthates and ditertiary phosphanes of the composition $Ni(ROCSS)_2(diphos)_2$ have been prepared, where R = methyl, ethyl, propyl, butyl, and cyclohexyl and diphos = bis(diphenylphosphino)ethane (dpe) and bis(diphenylphosphino)butane (dpb). The newly prepared compounds were characterized on the basis of chemical analyses, infrared and electronic spectra, ^1H-NMR, molar conductance, and thermal analysis. A square planar structure was proposed for the complexes.

INTRODUCTION

Current interest in simple and mixed metal complexes of xanthates stems from their importance as insecticides and fungicides,[1] their use in vulcanization of rubber,[2] as antioxidants,[3] and as lubricants[4]. For some years xanthato metal complexes have been extensively studied.[5] Xanthatonickel(II) complexes strongly interact with Lewis bases containing nitrogen, oxygen and phosphorous doner atoms.[6,7,8]

Furthermore, phosphorous ligands are known to be involved in various catalytic reactions of transition metals and the steric and electronic characters of these ligands are extremely important in such reactions.[9] To our knowledge no work has yet been done on the interaction of diphosphanes with alkylxanthatonickel(II). Therefore, we wish to report in this article the preparation and characterization of some new mixed ligand complexes of alkylxanthatonickel(II) and two ditertiary phosphanes *vz.* bis(diphenylphosphino)ethane (dpe) and bis(diphenylphosphino)butane (dpb).



R = methyl, Mexan;
= propyl, Prxan;
= cyclohexyl, Cyxan

R = ethyl, Etxan
R = butyl, Buxan

$Ph_2P—(CH_2)_2—PPh_2$
dpe

$Ph_2P—(CH_2)_4—PPh_2$
dpb

RESULTS AND DISCUSSION

The reaction of alkylxanthatonickel(II) with ditertiary phosphanes proceeds readily to give the corresponding mixed ligand complexes in high yield.

$$Ni(ROCSS)_2 + 2Ph_2P(CH_2)_nPPh_2 \rightarrow Ni(ROCSS)_2(Ph_2P(CH_2)_nPPh_2)_2 \quad (1)$$

(R = Me, Et, Pr, Bu and Cy; n = 2 or 4).

It is of interest to note that, although phosphanes and alkylxanthatonickel(II) were mixed in the molar ratio 1 : 1, only a 2 : 1 stoichiometry was obtained for the corresponding mixed ligand complexes.

The complexes are stable in air; they are soluble in chloroform, dimethylformamide, dimethylsulphoxide, insoluble in benzene, alcohol or acetone. The complexes are reported in Table I together with their analytical data, melting point and colour.

IR Data

Assignments are made on the basis of previously published IR data on metal complexes of xanthates and their mixed ligand complexes.[8,10,11,12] A band appears at 1180 cm^{-1} for all the complexes, which we assign to the C—O—C asymmetric stretching mode. This band comes at a considerably lower frequency than usual for alkylxanthatonickel(II) complexes.[10,12] This observation suggests a change of coordination mode of the alkylxanthates from bidentate to monodentate ligands upon interaction with phosphanes, which is in accord with previous reports.[8] Symmetric vibration of C—O—C occurs at about 1090 cm^{-1}. Further, the band observed in the region 1020—1030 cm^{-1} appears to be associated with the C=S frequency; this range is also exhibited by mixed ligand complexes containing monodentate xanthates.[8] We assign the band at 475 cm^{-1} as a bending mode of the ligands.[11] It could be inferred that the extra bands in the 700—780 cm^{-1}, absent in the spectra of xanthatonickel(II), are due to -CH_2(rocking) and PPh_2-frequencies of the coordinated phosphanes.[13]

Electronic Spectral Data

Pertinent absorption bands of chloroform solutions of the complexes together with their tentative assignments are shown in Table I. Two prominent bands are seen in the regions 18,100—20,010 and 21,210—23,240 cm^{-1} assignable to the d—d transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$, respectively. This may suggest a square planar configuration of the central atom.[14] The relatively high intensity of the two bands may be attributed to the strong π interaction of nickel-phosphorous and/or nickelsulphur bonds.[8,14] The spectra of the presently prepared complexes bear a remarkable resemblance to those reported for analogous dithiolatonickel(II) mixed ligand complexes,[13,15] for which a square planar stereochemistry was proposed. It seems reasonable to assign the bands in the range 25,000—27,710 cm^{-1} to charge transfer transitions while those in the region 31,540—32,250 cm^{-1} to a transition of the type $\pi - \pi^*$.

Addition of chloroform solutions of dpe and dpb in various molar ratios (*vz.* 1 : 0.5, 1 : 1, 1 : 1.5, 1 : 2, 1 : 3, 1 : 4) to chloroform solutions of the bis-

Compound	Analytical data			Colour	*m. p.* (C°)	Yield	Λ	Electronic spectra (cm^{-1})			
	C⁰/₀ (calc.)	H⁰/₀ (calc.)	S⁰/₀ (calc.)					$^1A_{1g} \rightarrow {}^1A_{2g}$	$^1A_{1g} \rightarrow {}^1B_{1g}$	CT	π—π^*
Ni(Mexan)$_2$(dpe)$_2$	(62.87) 63.20	(5.08) 5.14	(11.98) 11.00	light red	180 (decomp.)	80	14	18,100	21,210	25,630 27.720	32,200
Ni(Etxan)$_2$(dpe)$_2$	(63.45) 64.22	(5.31) 5.38	(11.68) 12.00	orange	190 (decomp.)	85	12	18,510	21,210	26,330 27,720	31,530
Ni(Prxan)$_2$(dpe)$_2$	(64.00) 64.94	(5.54) 5.74	(11.39) 11.28	orange	183 (decomp.)	80	11	18,110	21,250	26,330 27,710	32,24
Ni(Buxan)$_2$(dpe)$_2$	(64.53) 64.32	(5.76) 5.83	(11.11) 11.84	orange	192 (decomp.)	75	13	18,550	21,260	27,710	31,540
Ni(Cyxan)$_2$(dpe)$_2$	(65.72) 65.50	(5.84) 5.80	(10.63) 10.72	yellow	195 (decomp.)	65	13	19,220	21,540	27,710	32,220
Ni(Mexan)$_2$(dpb)$_2$	(64.00) 63.75	(5.54) 5.65	(11.39) 10.68	pale brown	210 (decomp.)	70	14	20,010	—	25,000 27,710	29,820 32,220
Ni(Etxan)$_2$(dpb)$_2$	(64.52) 64.21	(5.76) 5.51	(11.11) 10.89	grey	218 (decomp.)	73	12	—	23,210	27,010	31,750 32,220
Ni(Prxan)$_2$(dpb)$_2$	(65.03) 65.22	(5.96) 6.02	(10.84) 10.05	pale yellow	220 (decomp.)	63	13	—	23,240	27,010	31,730 32,250
Ni(Buxan)$_2$(dpb)$_2$	(65.50) 65.81	(6.16) 6.38	(10.59) 9.95	grey	213 (decomp.)	60	14	19,630	23,240	27,020	31,740 32,220
Ni(Cyxan)$_2$(dpb)$_2$	(66.60) 65.97	(6.22) 6.10	(10.16) 10.51	pale yellow	215 (decomp.)	62	13	18,830	21,270	27,020	32,250

(alkylxanthato)nickel(II) (at constant concentration of 5×10^{-3} M) causes a decrease in the absorbances of the xanthatonickel(II) spectra. A small red shift in the bands of the xanthatonickel(II) complexes was noticed (about 1,000 cm^{-1} for the system dpe/$Ni(ROCSS)_2$ and no appreciable shift was observed for the system dpb/$Ni(ROCSS)_2$, thus confirming the square planar structure of the resulting complexes. An isosbestic point appears in case of the system dpb/$Ni(ROCSS)_2$ suggesting the following equilibrium to occur:

$$Ni(ROCSS)_2 + 2Ph_2P(CH_2)_nPPh_2 \rightleftharpoons Ni(ROCSS)_2(Ph_2P(CH_2)_nPPh_2)_2 \qquad (2)$$

$n = 2$ or 4

Typical spectra of $Ni(Cyxan)_2$ plus dpb at different molar ratios are depicted in Figure 1. The plot of absorbance against molar ratio gives a break at 2 : 1 molar ratio indicating the formation of 2 : 1 mixed ligand complexes in solution. This is in contrast to the spectrophotometric titration (at the same molar ratios) of dithiocarbamato — and dithiocarbazatonickel(II)[16] with ditertiary phosphanes, where only 1 : 1 mixed ligand complexes were formed in solution (except for the system dpe/bis(phenyldithiocarbazato)nickel(II) which forms both 1 : 1 and 1 : 2 mixed ligand complexes in solution); it was suggested that the 2 : 1 mixed ligand complexes undergo a rapid dissociation to the 1 : 1 mixed ligand complexes.

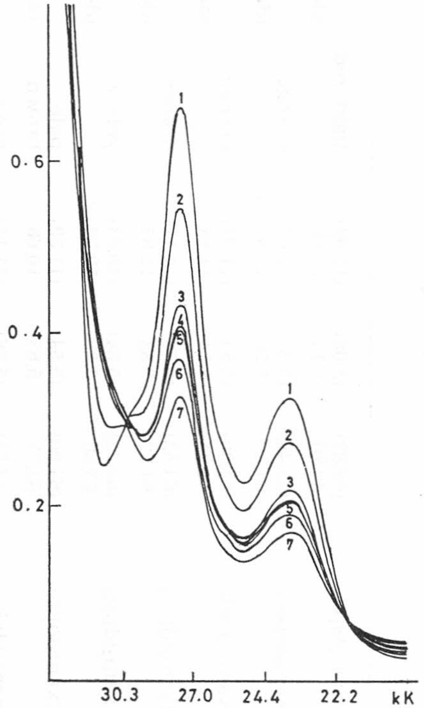


Figure 1. Absorption spectra of the system dpb/$Ni(Cyxan)_2$ at different molar ratios (ratio in parentheses): 1 (0 : 1); 2 (0.5 : 1); 3 (1 : 1); 4 (1.5 : 1); 5 (2 : 1); 6 (3 : 1); 7 (4 : 1).

Conductivity Data

Conductivity measurements in DMSO indicate that the complexes are essentially non-electrolytes (Table I).

^{1}H-NMR Data

The ^{1}H-NMR spectra of the complexes in deuterated chloroform show the protons of the phenyl groups of phosphanes (dpe and dpb) in the range δ 7.4—7.9 ppm as two sets of multiplets which integrate in the ratio 2 : 3; it suggests that *ortho*-proton signals appear down-field compared to meta — and *para* protons. In addition, in the region δ 1.0—4.3 ppm, the spectra show the characteristic resonances of the alkyl groups of xanthate ligands and the $-(CH_2)_n-$ of the phosphanes; the spectra are rather complicated in this region.

Thermal Data

The TGA curves of the complexes in the temperature range 100—700 °C consist of three stages of weight loss. The first weight loss occurs in the range 180—210 °C which is consistent with the elimination of an aldehyde molecule (eq. 3). Elimination of aldehydes during the thermal decomposition of xanthates is

$$Ni(ROCSS)_2(Ph_2P(CH_2)_nPPh_2)_2 \xrightarrow{-R'CHO} Ni(ROCSS)\,(HCSS)\,(Ph_2P(CH_2)_nPPh_2)_2 \qquad (3)$$

$n = 2$ or 4

known in the literature.[12] Beyond 210 °C decomposition continues with the loss of ligands up to 400 °C (second step). From this last temperature up to 700 °C the third decomposition step is observed; the end product is identified (on the basis of IR spectra) as $Ni_2P_2O_7$. A typical TGA thermogram of Ni(Mexan)$_2$(dpe)$_2$ is shown in Figure 2.

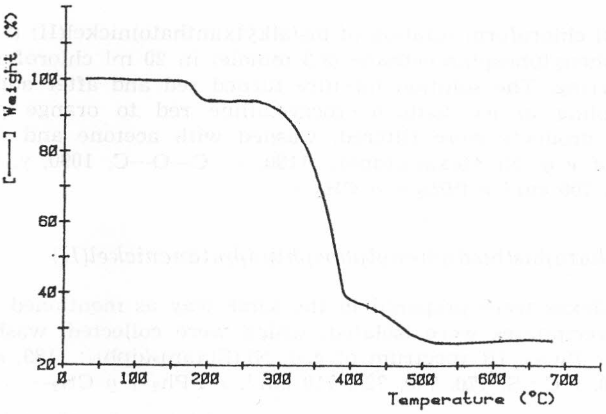
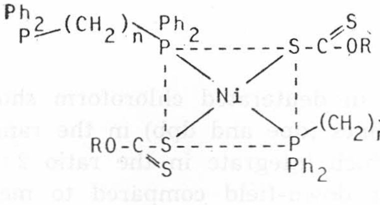
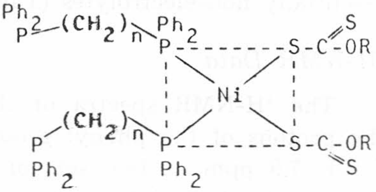


Figure 2. TGA thermogram of Ni(Mexan)$_2$(dpe)$_2$.

In view of the previous discussion it is to be concluded that the prepared complexes may have either of the following two structures:



(I)



(II)

Unfortunately, on the basis of the above data it is difficult to make a definite assignment of the possible structure of the complexes *i. e.* the *trans-(I)* or the *cis-(II)*-square planar geometry. The relatively high intensity of the d—d bands (*cf.* the electronic spectral data) may be in favour of the *cis*-form as it has a lower (local) symmetry than the *trans*-form.

Monodentate, mixed bidentate and monodentate, and mixed bidentate and bridging phosphanes are known in the literature for some nickel(II) phosphane complexes.[18]

EXPERIMENTAL

All chemicals were of analytical grade. The alkylxanthatonickel(II) precursors were prepared folloving published procedures.[5,19] IR spectra were obtained using potassium bromide pellets with a Perkin Elmer 599B recording spectrophotometer. Electronic spectra were obtained with a Shimadzu UV-200S and matched 1.0 cm quartz cells. Conductance measurements were made on fresh solutions (10^{-3} M) in a LF Digi 550 conductance bridge. Proton nuclear magnetic resonance spectra were recorded on a Varian EM-390 NMR 90 MHz spectrometer. Tetramethylsilane (TMS) was employed as an external standard. Thermal gravimetric analysis was determined with a 1090 Du pont thermal analyzer, with a furnace heating rate of 10 °C per minute.

Bis(alkylxanthato)bis(bisdiphenylphosphino)ethanenickel(II)

To a 20 ml chloroform solution of bis(alkylxanthato)nickel(II) (3.3 mmole) a solution of bis(diphenylphosphino)ethane (3.3 mmole) in 20 ml chloroform was added at continuous stirring. The solution mixture turned red and after addition of diethylether and cooling in ice bath microcrystalline red to orange precipitates were obtained. The products were filtered, washed with acetone and dried over P_4O_{10}. IR-spectrum of *e. g.* Ni (Mexan)$_2$(dpe)$_2$: 1180, ν_{as} C—O—C, 1090, ν_s C—O—C, 1020, ν C=S, 740, 710, 700 cm^{-1} ν PPh$_2$ + ϱ CH$_2$—.

Bis(alkylxanthato)bis(bisdiphenylphosphino)butanenickel(II)

The complexes were prepared in the same way as mentioned above. Yellow to pale brown precipitates were isolated, which were collected, washed with acetone and dried over P_4O_{10}. IR-spectrum of *e. g.* Ni (Etxan)$_2$(dpb)$_2$: 1189, ν_{as} C—O—C, 1095, ν_s C—OC, 1020, ν C=S, 770, 740, 720, 710 cm^{-1}, ν PPh$_2$ + ϱ CH$_2$—.

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SAŽETAK

Novi mješoviti kompleksi ditercijarnih fosfana s nikal(II)-alkilksantatima

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Pripravljani su mješoviti kompleksi nikla(II) s alkilksantatima i ditercijarnim fosfanima; opći im je sastav Ni(ROCSS)$_2$(diphos)$_2$ (R: Me, Et, Pr, Bu, cikloheksil; *diphos: bis(difenilfosfino)etan, bis(difenilfosfino)butan*).

Na osnovi elementne analize, elektronskih, vibracijskih i NMR spektara, kao i mjerenja vodljivosti i termičke analize, za te je komplekse predložena kvadratna planarna struktura.