Reactivity of Ethylenebis(dithiocarbamate) and Diethyldithiocarbamate Ligands towards Phosphine Complexes of Nickel(II)

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Mono- and poly-nuclear dithiocarbamate complexes of nickel(II) containing tertiary phosphines as ligands were obtained. Depending on the nature of the phosphine [PPh_3 or $Ph_2PCH_2CH_2PPh_2$ (dppe)] and the dithiocarbamate used [dedtc = diethyldithiocarbamate or ebdtc = ethylenebis(dithiocarbamate)], square-planar [$(Ph_3P)ClNi(\mu$-ebdtc$)NiCl(PPh_3)$], five-co-ordinate [Ni(ebdtc)(dppe)], and the unusual six-co-ordinate [$Ni(dedtc)_2(dppe)$] complexes were obtained.

The square-planar bis-dithiocarbamate complexes of nickel(II), [$Ni(dtc)_2$][1] (dtc = dialkyldithiocarbamate), as well as the related compounds containing tertiary phosphines, [$NiCl(dtc)(PR_3)$],[2] are well known.

Thompson and Moyer[3] and Kwoka *et al.*[4] described the bis-dithiocarbamate complexes with alkylenebis(dithiocarbamate) ligands. The reaction of $Na_2(ebdtc)\cdot6H_2O$ [ebdtc = ethylenebis(dithiocarbamate)] with nickel(II) salts gives rise to the complex [Ni(ebdtc)]$\cdot H_2O$.[3] This is a polymer built up of –Ni(ebdtc)– units, with the dithiocarbamate bidentate and bridging two metals. Barrientos *et al.*[5] deduced that the polymer has a medium length of 75 units.

We are interested in the study of the effect of S- and P-donor ligands on the environment of Ni^{II} atoms. We have previously reported[6] the formation of five-co-ordinate complexes [$Ni(S_2COR)_2(dppe)$] (R = cyclo-C_6H_{11}, dppe = $Ph_2PCH_2CH_2PPh_2$), unusual six-co-ordinate compounds [$Ni(S_2COR)_2L_2$] (R = cyclo-C_6H_{11}, L = dppe; R = Et, L = $PMePh_2$), and the square-planar dithiocarbonate [$Ni(S_2CO)(dppe)$]. All of these compounds were obtained by the reaction of [$Ni(S_2COR)_2$] with the phosphine ligands. In contrast to this behaviour [$Ni(dtc)_2$] complexes do not react with nucleophiles.

We present here the preparation of the nickel complexes containing ebdtc as the ligand as well as a study of the reactivity of dedtc (dedtc = diethyldithiocarbamate) and ebdtc towards [$NiCl_2(PPh_3)_2$] and [$NiCl_2(dppe)$].

Results and Discussion

The substitution of the sodium cation by the tetraphenylphosphonium cation in $Na_2(ebdtc)\cdot6H_2O$ forms the yellow salt $[PPh_4]_2$[ebdtc] (1). The i.r. spectrum shows the characteristic stretch of dithiocarbamates, ν(CN) at 1 460 cm^{-1}, in the region of monodentate dithiocarbamates, and 40 cm^{-1} lower than in $Na_2(ebdtc)\cdot6H_2O$. This fact, along with a low value for the electrical conductivity, seems to indicate that some interaction occurs between the phosphorus atom and one of the sulphur atoms of the dithiocarbamate.

The reaction of (1) with $NiCl_2\cdot6H_2O$ gives rise to a green solid. This solid shows an i.r. spectrum and analytical data which suggest the formation of $[PPh_4]_2[Ni_n(ebdtc)_{n+1}]$ (2), which has a medium value of $n = 3.5$. The bulky cation $[PPh_4]^+$ probably brings about a lower degree of polymerization due to an increase in the complex insolubility. This complex shows a ν(CN) band at 1 510 cm^{-1}, similar to that of [Ni(ebdtc)]$\cdot H_2O$,[3] showing bidentate co-ordination. The electronic spectrum corresponds to a square-planar environment.

The reaction of $Na_2(ebdtc)\cdot6H_2O$ and the tetrahedral [$NiCl_2(PPh_3)_2$] has as its major product [Ni(ebdtc)]$\cdot H_2O$, along with a brown solid identified as [$(Ph_3P)ClNi(\mu$-ebdtc$)NiCl(PPh_3)$] (3). This compound is closely related to the reported complex [$NiCl(dedtc)(PPh_3)$].[2] The electronic spectrum of (3) corresponds to a square-planar co-ordination of the nickel, with the ebdtc ligand bidentate and acting as a bridge between the two metals.

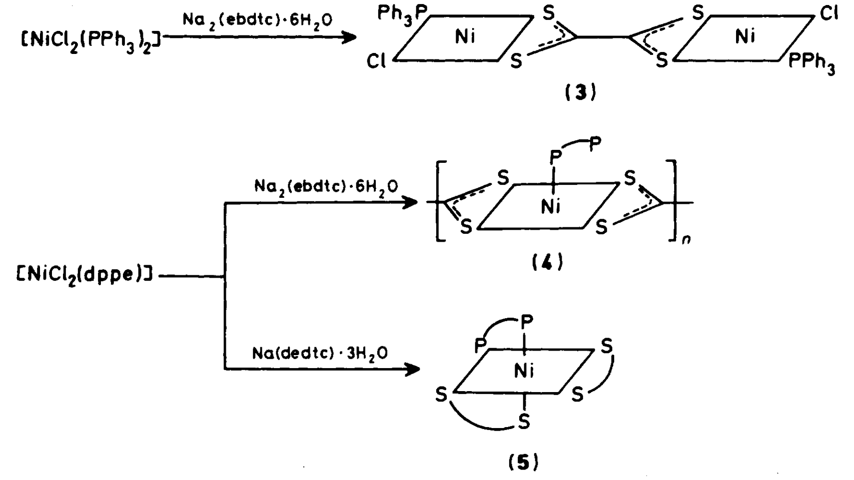
When [$NiCl_2(dppe)$] reacts with $Na_2(ebdtc)\cdot6H_2O$ a brown solid, [Ni(ebdtc)(dppe)] (4), is obtained. This complex is diamagnetic and its electronic spectrum probably indicates low-spin five-co-ordination. The product can be regarded as built up of –Ni(ebdtc)(dppe)– units, with the nickel atoms in a square-pyramidal (SSSSP) environment.[7]

A similar reaction occurs in the interaction of [$NiCl_2(dppe)$] with $Na(dedtc)\cdot3H_2O$, having as its main product [$Ni(dedtc)_2$]. In the same reaction, an orange solid identified as [$Ni(dedtc)_2(dppe)$] (5) is isolated. Its i.r. spectrum indicates bidentate co-ordination of the dithiocarbamate. The diffuse reflectance spectrum corresponds to a six-co-ordinate complex, with the phosphine in a bidentate co-ordination. The absorption maxima at *ca.* 900, 630, and 485 nm can be attributed to the three *d–d* transitions of pseudo-octahedral complexes. These bands shift to lower frequencies with respect to the analogous bis(dithiocarbonate) [$Ni(S_2COC_6H_{11})_2(dppe)$][6] in accordance with the higher ligand-field strength of dithiocarbonates.[8] The complex (5) is a non-conductor in solution and its effective magnetic moment, 2.85, is characteristic of octahedral nickel(II). Complexes (3), (4), and (5) are shown in the Scheme.

The observed formation of [Ni(ebdtc)]$\cdot H_2O$ or [$Ni(dedtc)_2$] in the reactions described is consistent with the partial or total substitution of phosphine ligands. We have tried to make use of the aforesaid in order to obtain mixed dithiocarbamate complexes from the reaction of [$NiCl(dedtc)(PPh_3)$] with $Na_2(ebdtc)\cdot6H_2O$. All these attempts have failed and the reaction occurs with displacement of the chlorine and phosphine giving rise to a mixture of [$Ni(dedtc)_2$] and [Ni(ebdtc)]$\cdot H_2O$.

Experimental

All reactions were carried out under oxygen-free nitrogen, the products obtained being stable to air and moisture. The compounds $Na_2(ebdtc)\cdot6H_2O$,[3] [$NiCl(dedtc)(PPh_3)$],[2] [$NiCl_2(PPh_3)_2$],[9] and [$NiCl_2(dppe)$][10] were prepared by the reported methods. Analyses were performed by the Centro Nacional de Química Orgânica, Consejo Superior de Investigaciones Cientifices (Madrid). I.r. spectra were recorded on a Perkin-Elmer 325 spectrophotometer with KBr pellets. Electronic spectra, in solution or in $BaSO_4$ dispersion, were recorded on a Uvikon 620 spectrophotometer. Conductivity measurements were made on a Phillips PR 9512/00 apparatus.



Scheme. Products of the reactions with phosphine complexes

Magnetic susceptibilities were measured by the Faraday method on a Sartorius microbalance using a Bruker BM4 electromagnet.

Bis(tetraphenylphosphonium) Ethylenebis(dithiocarbamate) (**1**).—Addition of [PPh$_4$]Cl (1 g) in water (10 cm^3) to a solution of Na$_2$(ebdtc)·6H$_2$O (0.4 g) in water (20 cm^3) resulted in formation of a yellow precipitate of [PPh$_4$]$_2$[ebdtc] (**1**). The solid was filtered off, washed with water, and dried *in vacuo*. Yield 85%, m.p. 174—176 °C (Found: C, 69.1; H, 5.05; N, 3.30; S, 16.3. $C_{52}H_{46}N_2P_2S_4$ requires C, 68.8; H, 5.10; N, 3.10; S, 14.15%). $\nu_{max.}$(CN) 1 460s cm^{-1}; $\lambda_{max.}$(MeOH) 470 (lg ε 1.78), 335 (3.59), 287 (4.29), 275 (4.34), and 260 nm (4.40); Λ_M(MeOH) 120 Ω^{-1} cm^2 mol^{-1}.

Reaction of (**1**) *with Nickel*(II) *Salts*.—Complex (**1**) (0.5 g) in methanol (15 cm^3) was added to a methanolic solution (25 cm^3) of NiCl$_2$·6H$_2$O (0.13 g) [or 0.1 g of nickel(II) acetate]. A dark green solid, [PPh$_4$]$_2$[Ni$_n$(ebdtc)$_{n+1}$] (**2**) (n = 3.5), was immediately formed. The product was filtered off, washed with methanol and diethyl ether, and dried. Yield 87%, m.p. 174 °C (decomp.) (Found: C, 42.4; H, 3.15; N, 6.75; Ni, 11.2; S, 32.1. $C_{66}H_{67}N_9Ni_{3.5}P_2S_{18}$ requires C, 42.8; H, 3.65; N, 6.80; Ni, 11.1; S, 31.2%). $\nu_{max.}$(CN) 1 510s cm^{-1}; $\lambda_{max.}$(Me$_2$SO) 625 [lg ε 1.87, $^1A_{1g} \rightarrow {}^1B_{1g}$ (symmetry D_{4h})], 480 [2.26, $^1A_{1g} \rightarrow {}^1A_{2g}$ (symmetry D_{4h})], 420 (3.09), 375 (3.64), and 325 nm (4.42).

Reaction of Na$_2$(ebdtc)·6H$_2$O *with* [NiCl$_2$(PPh$_3$)$_2$].—A solution of Na$_2$(ebdtc)·6H$_2$O (2.1g) in ethanol (50 cm^3) was added to a stirred suspension of [NiCl$_2$(PPh$_3$)$_2$] (5 g) in hot ethanol (50 cm^3). The solution turned red and a brown precipitate was formed. This solid was extracted with hot acetone, leaving a green residue of [Ni(ebdtc)]·H$_2$O. By the addition of n-hexane to the acetone solution, a brown precipitate of [(Ph$_3$P)ClNi(μ-ebdtc)NiCl(PPh$_3$)] (**3**) was separated. Yield 12%, m.p. 180—183 °C (decomp.) (Found: C, 50.2; H, 3.60; N, 3.25; Ni, 11.9; S, 14.7. $C_{40}H_{36}Cl_2N_2Ni_2P_2S_4$ requires C, 51.0; H, 3.85; N, 2.95; Ni, 12.5; S, 13.6%). $\nu_{max.}$(CN) 1 520s cm^{-1}; $\lambda_{max.}$(Me$_2$CO) 610 [lg ε 2.08, $^1A_{1g} \rightarrow {}^1B_{1g}$ (symmetry C_{4v})], 515 [2.67, $^1A_{1g} \rightarrow {}^1A_{2g}$ (symmetry D_{4h})], 425 (2.86), 380 (3.52), and 330 nm (3.96); Λ_M(Me$_2$CO) 0.14 Ω^{-1} cm^2 mol^{-1}.

Reaction of Na$_2$(ebdtc)·6H$_2$O *with* [NiCl$_2$(dppe)].—A solution of Na$_2$(ebdtc)·6H$_2$O (0.26 g) in methanol (10 cm^3) was added to a stirred suspension of [NiCl$_2$(dppe)] (0.5 g) in hot methanol (20 cm^3). The orange [NiCl$_2$(dppe)] disappeared and after 3 min, a brown precipitate of [Ni(ebdtc)(dppe)] (**4**) was formed. The solid was washed with methanol and diethyl ether. Yield 65%, m.p. 208—210 °C (decomp.) (Found: C, 53.6; H, 4.15; N, 4.00; Ni, 9.8; S, 18.7. $C_{30}H_{30}N_2NiP_2S_4$ requires C, 52.5; H, 4.4; N, 4.1; Ni, 8.6; S, 18.7%). $\nu_{max.}$(CN) 1 530vs cm^{-1}; $\lambda_{max.}$(CHCl$_3$) 670 [lg ε 2.41, $^1A_1 \rightarrow {}^1B_1$ (symmetry C_{4v})], 520 [2.40, $^1A_1 \rightarrow {}^1A_2$ (symmetry C_{4v})], 425 (2.52), 380 (3.41), and 325 nm (3.96); Λ_M(CHCl$_3$) 0.72 Ω^{-1} cm^2 mol^{-1}.

Reaction of Na(dedtc)·3H$_2$O *with* [NiCl$_2$(dppe)].—A solution of Na(dedtc)·3H$_2$O (1.14 g) in n-butanol (10 cm^3) was added to a stirred suspension of [NiCl$_2$(dppe)] (1.32 g). The solution immediately became red and a green precipitate of [Ni(dedtc)$_2$] was formed. This solid was filtered off and the solution cooled overnight. A brown precipitate was produced. By dissolving this solid in acetone more [Ni(dedtc)$_2$] was separated. The acetone solution was concentrated to 10 cm^3 and by the addition of diethyl ether, orange microcrystals of [Ni(dedtc)$_2$(dppe)] (**5**) appeared. Yield 32%, m.p. 268 °C (Found: C, 55.3; H, 5.60; N, 3.25; Ni, 7.7; S, 14.7. $C_{36}H_{44}NiP_2S_4$ requires C, 56.0; H, 5.75; N, 3.65; Ni, 7.6; S, 16.7%). $\nu_{max.}$(CN) 1 530s cm^{-1}; $\lambda_{max.}$(CHCl$_3$) *ca.* 900 [solid, $^3A_{2g} \rightarrow {}^3T_{2g}$ (symmetry O_h)], 630 [lg ε 1.38, $^3A_{2g} \rightarrow 3T_{1g}$ (symmetry O_h)], 485 [2.38, $^3A_{2g} \rightarrow {}^3T_{1g}$ (symmetry O_h)], 420 (2.86), and 380 nm (3.32); Λ_M(CHCl$_3$) 1.7 Ω^{-1} cm^2 mol^{-1}; $\mu_{eff.}$ 2.85.

Reaction of Na$_2$(ebdtc)·6H$_2$O *with* [NiCl(dedtc)(PPh$_3$)].—A solution of [NiCl(dedtc)(PPh$_3$)] (0.5 g) and Na$_2$(ebdtc)·6H$_2$O (0.18 g) in methanol (20 cm^3) was stirred for 1 h. A green precipitate was formed and by extraction with hot chloroform a green solution and a green solid were produced. The solid was identified as [Ni(ebdtc)]·H$_2$O. On addition of n-hexane to the solution a green solid precipitated, which was analysed as [Ni(dedtc)$_2$].

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