A Novel Series of Transition-metal Chelates of Diphenylphosphinothioylthiourea Anion

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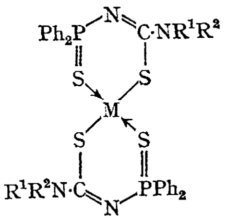
Summary Two thiourea derivatives, 3-(diphenylphosphinothioyl)-1-phenylthiourea and 3-(diphenylphosphinothioyl)-1,1-diethylthiourea, behave as bidentate ligands towards Ni^{II} and Pd^{II} to produce new square-planar complexes, while the latter ligand gives a tetrahedral complex with Co^{II}.

THE thiourea derivatives, 3-(diphenylphosphinothioyl)-1-phenylthiourea(PTTU-A) and 3-(diphenylphosphinothioyl)-1,1-diethylthiourea(PTTU-B), obtained by addition of diphenylphosphinothioyl isothiocyanate with aniline and diethylamine, respectively, react with bivalent metal halides to give a series of novel metal chelates.

A solution of PTTU-B (4 mmoles) in dichloromethane (20 ml.) was allowed to react with nickel(II) chloride hexahydrate (2 mmoles) in ethanol at room temperature. The precipitate thus formed was recrystallized from dichloromethane–ethanol solution. A crystalline bis-[3-(diphenylphosphinothioyl)-1,1-diethylthioureato]nickel(II) (Ni-PTTU-B) was obtained in nearly quantitative yield. The Ni^{II} and Pd^{II} complexes of PTTU-A and the Pd^{II} and Co^{II} complexes of PTTU-B were prepared in a similar way. Ni-PTTU-A: dark green needles, m.p. 193° (dec.), λ_{max} (CH_2Cl_2) 15·7 (log ϵ 2·36), 18·0 kK(2·30). Pd-PTTU-A: orange-yellow prisms, m.p. 215° (dec.). Ni-PTTU-B: dark green needles, m.p. 200° (dec.), λ_{max} (CH_2Cl_2) 15·5(2·24) and 17·6 kK(2·24). Pd-PTTU-B: pale-yellow prisms, m.p. 244° (dec.). Co-PTTU-B: bright green needles, m.p. 205—206°, χ_g = 11·9 c.g.s. e.m.u. (room temp.), λ_{max} (CH_2Cl_2) 4·65 (1·50), 7·87(2·41), 14·3(2·57), and 15·7 kK(2·54).



M-PTTU-A: R^1=Ph, R^2=H
M-PTTU-B: R^1=R^2=Et
M=Ni, Pd, Co

The elemental analyses for these complexes were in good agreement with calculated values. All these complexes have the same metal : ligand ratio (1 : 2). Their solubilities in benzene were not high enough for us to determine their molecular weights except for the case of Co-PTTU-B, *M* (found) 751; calc. for monomer: 753. Except for Co-PTTU-B, they are all diamagnetic at room temperature, which suggests that the complexes of Ni^{II} and Pd^{II} have square-planar configurations. Their crystal structures appear to be isomorphous according to the powder *X*-ray diffraction patterns.

The effective magnetic moment of Co-PTTU-B, $\mu_{eff.} = 4{\cdot}50$ B.M., corresponds to the high-spin state of d^7 Co^{II} in a tetrahedral configuration. Its powder *X*-ray diffraction pattern was quite different from those of Ni- and Pd-PTTU-B. The electronic spectrum also supported the tetrahedral configuration of Co^{II} in Co-PTTU-B. The values of *B* (684 cm.$^{-1}$) and 10 *Dq* (4788 cm.$^{-1}$) calculated on the basis of the Tanabe–Sugano diagram, are in reasonable agreement with those reported on several tetrahedral Co^{II} complexes.[1] Cobalt(II) in Co-PTTU-B has a tetrahedral configuration, in contrast with the case of bis(dithioacetylacetonato)cobalt(II), which has a square-planar structure.[2]

In the i.r. spectra of the chelates with the square-planar structure, two metal–sulphur stretching vibrations were expected to appear in the far-i.r. region.[3] The bands most sensitive to metals, appearing in the region 420—320 cm.$^{-1}$, are tentatively assigned to these vibrations in view of the covalent nature of the metal–sulphur bond and the mass effect (Table). The tentative assignments of P=S stretching bands are also given in the Table.

Characteristic bands in the far-i.r. spectra (cm.$^{-1}$)

	P=S	M–S(1)	M–S(2)
Ni-PTTU-A	584	417	358
Pd-PTTU-A	582	412	336
Ni-PTTU-B	580	391	340
Pd-PTTU-B	579	380	329

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