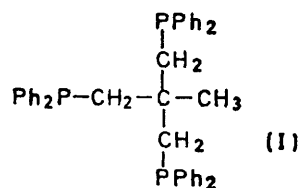


Halogeno-complexes of Cobalt(I) and Nickel(I) with 1,1,1-tris(diphenylphosphinomethyl)ethane

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The terdentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (I) forms cobalt- and nickel-(I) complexes of general formula MLX (X = Cl, Br, or I). Spectral and magnetic data on the compounds are presented. They are non-electrolytes, are all isomorphous (X-rays) with the analogous Cu^I complexes, and probably have a pseudo-tetrahedral structure.

RELATIVELY few cobalt(I) complexes have been described to date, and those of nickel(I) are very rare. Leaving aside the carbonyl derivatives, the most important group of cobalt(I) complexes is that of the compounds formed with uni- and bi-dentate ligands having as donor atoms either phosphorus [1,2-bis(diphenylphosphino)-



ethane,¹ triphenylphosphine,² or triethyl phosphite³] or nitrogen in a strongly conjugated system (2,2'-bipyridyl,^{4,5} o-phenanthroline,⁵ or terpyridyl⁵). For nickel(I) only a few compounds with cyanide,⁶ triphenyl-

¹ A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Comm.*, 1966, 589.

² M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 1969, **3**, 227.

³ M. E. Vol'pin and I. S. Kolomnikov, *Doklady Akad. Nauk. S.S.S.R.*, 1966, **170**, 1321.

⁴ B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207; G. M. Waind and B. Martin, *ibid.*, 1958, **8**, 551; A. A. Vlecek, *Nature*, 1957, **180**, 753.

phosphine,⁷ and ditertiary phosphines⁸ have been described. These compounds were prepared either by reduction of the bivalent metal complexes, or by oxidation of the zerovalent metal compounds, or by disproportionation reactions.

We have found that treatment of solutions of the complexes formed between cobalt- and nickel-(II) halides and the potentially terdentate tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (I; L), with sodium borohydride, at room temperature, gives four-coordinate metal(I) complexes of general formula MLX (X = Cl, Br, or I). The iodide compounds can be obtained even in the absence of external reducing agents. The reducing behaviour of tertiary phosphines on metal halides, where the metal is in a 'high' oxidation state, is well known in the case of the elements of Group IB.⁹

The complexes of (I) which have been previously

⁵ H. Behrens and W. Aquila, *Z. anorg. Chem.*, 1967, **8**, 356.

⁶ R. Nast and T. von Krakkay, *Z. Naturforsch.*, 1954, **9b**, 798.

⁷ P. Heimbach, *Angew. Chem. Internat. Edn.*, 1964, **3**, 648; L. Porri, M. C. Gallazzi, and G. Vitulli, *Chem. Comm.*, 1968, 509.

⁸ B. Corain, M. Bressan, P. Rigo, and A. Turco, *Chem. Comm.*, 1968, 509.

⁹ F. H. Jardine, L. Rule, and A. G. Vohra, *J. Chem. Soc. (A)*, 1970, 238.

described are those of cobalt(II),¹⁰ nickel(II),¹⁰ and nickel(0).¹¹ For purposes of comparison we have also prepared the corresponding complexes of copper(I).

EXPERIMENTAL

Preparation of the Ligand.—The ligand was prepared by the method previously described.¹²

Preparation of the Cobalt and Nickel Complexes.—All the complexes were prepared by the same method under nitrogen. The ligand (1 mmole) dissolved in methylene chloride (50 ml) was added in small portions to a solution of the anhydrous metal salt (1 mmole) in absolute ethanol (10 ml). To the resulting solution sodium borohydride (1 mmole) dissolved in ethanol (10 ml) was added dropwise, the solution being shaken vigorously after each addition. After the sodium halide had been filtered off, a brisk current of nitrogen was passed through the solution and the methyl-

ethane. On exposure to air the solids oxidize rapidly, their solutions even more so. Even solutions prepared in an inert atmosphere slowly become opalescent, probably because of disproportionation reactions similar to those found to occur with the triphenylphosphine-cobalt(I) complexes. This decomposition can be limited to a considerable extent by the addition of free ligand to the solutions. The iodo-complexes are much more stable than the bromo- and chloro-complexes, as might have been expected from the fact that they are prepared by direct reaction of the ligand with the metal(II) salt. All the compounds are non-conductors in 1,2-dichloroethane solution.

The copper(I) compounds are colourless, crystalline materials, soluble in non-polar organic solvents in which they are monomeric and non-conductors.

TABLE 1

Analytical and magnetic data for the complexes MLX

Compound	Colour	μ_{eff} B.M. ^a	% M ^b	% C	% H	% P
CoClCl ^c	Brick	3.06(27)	8.2(8.1)	68.5(68.1)	5.45(5.35)	12.9(13.05)
CoLBr	Brick	3.08(28)	7.7(7.7)	64.5(64.95)	5.15(5.45)	12.1(12.2)
CoLI	Brick red	3.03(28)	7.25(7.1)	60.75(62.6)	4.85(4.95)	11.45(11.55)
NiLCl ^d	Orange	1.98(29)	8.15(8.05)	68.5(68.1)	5.45(5.45)	12.9(12.85)
NiLBr	Yellow	1.97(31)	7.7(7.45)	64.5(65.1)	5.15(5.25)	12.2(12.1)
NiLI	Yellow	1.93(28)	7.25(7.1)	60.75(60.8)	4.85(5.0)	11.45(11.35)

^a Temp. (°C) in parentheses. ^b Found values in parentheses. ^c Cl: calc. 4.95, found 4.7. ^d Cl: calc. 4.9, found 4.9.

ene chloride evaporated until crystallisation commenced. The crystalline precipitate was filtered on a glass sinter, washed with absolute alcohol, water, alcohol again, and then light petroleum ether, and dried in a current of nitrogen.

The iodo-complexes were obtained without the use of sodium borohydride by gently heating the reaction mixture. The complex NiLI was prepared even by oxidation with iodine of the NiL₂ compound,¹¹ in a methylene chloride solution.

Preparation of the Copper Complexes.—The compounds CuLX (X = Cl, Br, or I), were obtained by the method described for the preparation of the compounds Cu(PPh₃)₃X.⁹ CuLCl requires: C, 68.0; H, 5.45; Cl, 4.9%; M.W., 723.7; Found: C, 67.2; H, 5.8; Cl, 4.95%; M.W. (in 1,2-dichloroethane) 719. CuLBr requires: C, 64.05; H, 5.1%; M.W., 768.1; Found: C, 63.45; H, 5.35%; M.W. (in 1,2-dichloroethane) 720. CuLI requires: C, 60.35; H, 4.8%; M.W., 815.1; Found: C, 60.05; H, 5.15%; M.W. (in 1,2-dichloroethane) 782

Materials and Physical Measurements.—All solvents were purified and dried by standard procedures. Physical measurements were carried out as previously described,¹³ and were made in an atmosphere of either nitrogen or argon.

RESULTS AND DISCUSSION

The analytical and magnetic data for the cobalt and nickel complexes are shown in Table 1. All the compounds are crystalline and are soluble in organic solvents such as benzene, methylene chloride, and 1,2-dichloro-

* It was not possible to obtain X-ray data for the nickel chloro-complex because it decomposed rapidly when exposed to X-rays.

¹⁰ R. Davis and J. E. Fergusson, *Inorg. Chim. Acta*, 1970, **4**, 23.

The spectral data for the solid compounds and their solutions in 1,2-dichloroethane are shown in Table 2 and Figures 1 and 2. All the spectra for the solid compounds of a given metal are very similar and are the

TABLE 2

Spectroscopic data ^a for the cobalt(I) and nickel(I) complexes

Compound	ν_{max} /kK (ϵ_{mol} for soln. in parentheses)
CoLCl	8.2, 9.0sh, 12.0, 19.6sh 8.3(445), 9.0sh, 12.0(198), 17.4sh
CoLBr	8.0, 9.0sh, 11.6, 20.4sh 8.1(558), 8.8sh, 11.9(211), 19.0sh
CoLI	7.7, 8.5sh, 11.3, 20.0sh 8.0(605), 8.6sh, 11.6(309), 20.0sh
NiLCl	7.3sh, 9.5, 15.0sh, 23.0sh 9.7(139), 15.0sh(?)
NiLBr	7.2sh, 9.3, 15.0sh, 25.0sh 9.65(247), 15.0sh(?)
NiLI	6.9sh, 9.1, 14.3sh, 18.2sh(?), 26.3sh 9.5(280), 14.5sh

^a Upper line, diffuse reflectance spectrum of solid; lower line, spectrum of solution in 1,2-dichloroethane.

same in solution. The spectrochemical-frequency shift Cl > Br > I is indicative of halide co-ordination, whilst the band intensity increases in the order Cl < Br < I, that is, with the polarisability of the anion.

The X-ray powder patterns of all the complexes are practically identical.*

For a given halogen the i.r. spectra (recorded as Nujol mulls) of all three complexes are very similar and only

¹¹ J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 1962, 2537.

¹² W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1962, 1490.

¹³ L. Sacconi and R. Morassi, *J. Chem. Soc. (A)*, 1968, 2997; L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 1968, **7**, 1417.

differ in the low-frequency region. No evidence was found in the 1700–2200 cm^{-1} region of absorption which could be attributed to hydridic hydrogens.

Cobalt Complexes.—These complexes all have essentially the same stereochemistry. Since they are non-conductors and can be assumed to be monomeric, as they

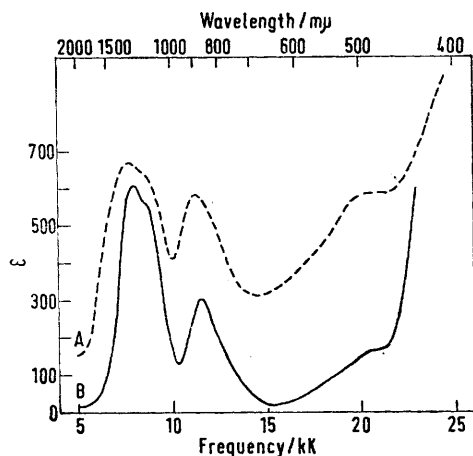


FIGURE 1 Electronic spectra of CoLI complex: A, diffuse reflectance; B, methylene chloride solution

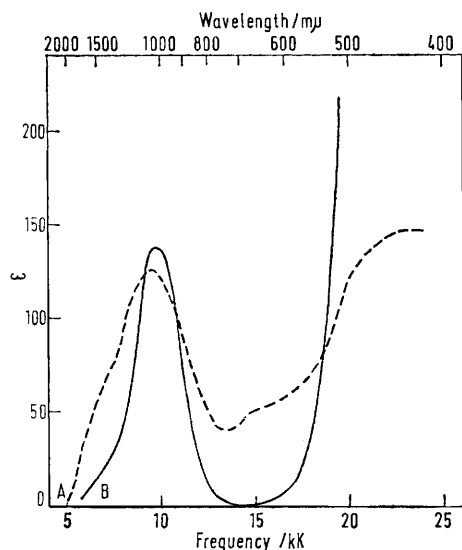


FIGURE 2 Electronic spectra of NiLCl complex: A, diffuse reflectance; B, methylene chloride solution

are isomorphous with the monomeric copper complexes, they must be four-co-ordinate with the phosphine acting as tridentate ligand. The room-temperature magnetic moments (3.03–3.09 B.M., Table 1), seem rather low for d^8 tetrahedral complexes, even if very much distorted.¹⁴ However these low values for μ_{eff} are not really abnormal considering the nature of the donor atom in these compounds. Indeed it has been shown¹⁵ that low values

¹⁴ B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 207.

¹⁵ B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. (A)*, 1966, 1411.

of μ_{eff} (room temperature) for pseudo-tetrahedral nickel(II) complexes can be mainly attributed to a reduction of the electronic delocalisation parameter; this is particularly marked when halogens are replaced by phosphorus atoms of the phosphine ligands in the co-ordination sphere. This is evident in the series of pseudo-tetrahedral compounds NiBr_4^{2-} , $\text{Ni}(\text{PPh}_3)\text{Br}_3^-$, and $\text{Ni}(\text{PPh}_3)_2\text{Br}_2^-$ which have room-temperature μ_{eff} 3.80, 3.60, and 3.27 B.M., respectively. Between 84 and 295 K the magnetic susceptibility of the cobalt bromo-complex follows the Curie–Weiss law with $\Theta = 0$. The negligible variation of the magnetic moment with temperature shows that the ligand field departs appreciably from tetrahedral symmetry in these complexes.¹⁵

The electronic spectra of these complexes show essentially three $d-d$ transitions: a band at 7.7–8.3 with a shoulder at 8.6–9.0, a sharp, less intense band at 11.3–12.0, and a shoulder at 17.4–20.0 kK. The high intensity of the bands with values from 200 to 600 is indicative of a non-centrosymmetric structure. The spectra of low-symmetry tetrahedral nickel(II) complexes show one or more bands < 9.0 kK which can be assigned to components of the ν_1 transition [${}^3T_1(F) \rightarrow {}^3T_2(F)$], a band at 10.0–12.0 kK corresponding to the ν_2 transition [${}^3T_1(F) \rightarrow {}^3A_2(F)$] which is not split since the excited state is orbitally nondegenerate even in a cubic field, and finally a poorly resolved envelope at 15.0–20.0 kK corresponding to the ν_3 transition [${}^3T_1(F) \rightarrow {}^3T_1(P)$].¹⁶ The ν_2 transition, which in the strong-field limit is a two-electron jump, is expected to be weaker than the other two, even though in a low-symmetry tetrahedral field its relative intensity can increase considerably. Taking these facts into consideration, it would seem that the spectra of our complexes are compatible with a d^8 pseudo-tetrahedral configuration with large low-symmetry components in the ligand field. However at present it is not possible to make an exact assignment of the absorption bands.

The (triphenylphosphine)cobalt(I) complexes,² to which a distorted tetrahedral structure has been assigned, have μ_{eff} values only slightly higher than those of our complexes (3.1–3.3 B.M. at room temperature, 3.04–3.08 B.M. at 77 K). However their electronic spectra are not very similar to those of our cobalt-complexes, as would have been expected in view of the identical donor atom sets in the two groups of compounds, and this must be attributed to the steric requirements of the ligand (I) in which the three phosphorus atoms are prevented from getting very far apart.

Nickel Complexes.—The marked similarity between the X-ray powder patterns and i.r. spectra of these compounds and those of the corresponding cobalt(I) complexes suggest that the co-ordination geometry in the two series of complexes is substantially the same, *i.e.* distorted tetrahedral.

The room-temperature magnetic moments are in the range 1.93–1.98 B.M. as expected or a d^9 configuration

¹⁶ L. Sacconi, 'Transition Metal Chemistry,' ed. R. L. Carlin, Dekker, New York, 1968, **4**, 199, and references therein.

with a small orbital contribution.¹⁷ Between 295 and 84 K the magnetic susceptibility of the complex NiLBr was found to follow the Curie-Weiss law with $\Theta = 0$.

The electronic spectra have a band at 9.1—9.7 with a slight shoulder at 6.9—7.3, a shoulder at 14.3—15.0, and a shoulder at 23.0—26.3 kK (Table 2 and Figure 2). These spectra are completely different, both as regards shape and band position, from those of the diphosphine compounds Ni(diphos)_{1,5}CN (diphos = 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane)⁸ which have been assigned a square-planar

structure. They are comparable with the spectra of distorted tetrahedral copper(II) complexes;¹⁸ however, at the present time, any attempt to assign the bands would be hazardous.

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¹⁷ B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 209.

¹⁸ I. Bertini and F. Mani, *Inorg. Chem.*, 1967, **6**, 2032.