*Inorganica Chimica Acta*, 43 (1980) 223–228

# Cobalt(II) and Nickel(II) Complexes with Tris(2-diethylphosphinoethyl)amine. Crystal and Molecular Structure of the Trinuclear Complex $[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$

C. BIANCHINI, C. MEALLI, A. MELI and L. SACCONI*

*Istituto di Chimica Generale ed Inorganica dell'Università, Istituto CNR, Via J. Nardi 39, Florence, Italy*
Received May 23, 1980

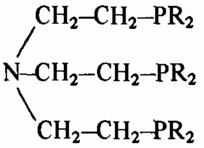
---

*The new ligand tris(2-diethylphosphinoethyl)amine, $N(CH_2CH_2P(C_2H_5)_2)_3$, Etnp$_3$, has been synthesized. It forms with cobalt(II) and nickel(II) salts different types of complexes depending on the reaction conditions.*

*The crystal and molecular structure of the $[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$ complex has been determined by standard X-ray methods, and refined to* R = *0.079. The crystals are monoclinic, space group* $P2_1/n$. *The unit cell dimensions are:* a = *20.067(5),* b = *17.555(5),* c = *12.652(4)* Å, β = *95.36(9)°*, Z = *4. The structure of the complex cation consists of three four-coordinated nickel atoms with square planar geometry. Two Etnp$_3$ ligands cement together these three metal centers. Chlorine atoms also enter in the coordination sphere of each nickel atom.*

## Introduction

In the course of previous studies performed in this Laboratory the coordinating behaviour of potentially tetradentate ligands of tripod form (I) toward 3d metals has been widely investigated


(I)

When R = Ph the ligand forms generally mononuclear metal complexes with coordination numbers ranging from four to six and geometries approaching the idealized forms of the trigonal pyramid [1], trigonal bipyramid [2], square pyramid [3], or octahedron [4].

In some cases the nitrogen atom is not coordinated to the metal so that a tetrahedral geometry of the complex is obtained [5].

When R = $CH_3$, invariably radial trinuclear complexes are formed, which contain the metal centers five-coordinated by the $NP_3$ donor atoms of one ligand and by a phosphorus atom of a central flattened ligand [6].

It seemed of interest, therefore, to investigate the effect of increasing the bulkiness of the alkyl groups

TABLE I. Analytical and Physical Data of the Complexes.

| Compound | % Calcd. | | | | % Found | | | | $\mu_{eff}$, $\mu_B$ (293 K) | $\Lambda_M$[a] cm$^2$ ohm$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | M | C | H | N | M | | |
| $[Ni(Etnp_3)Cl]BPh_4$ | 64.77 | 8.02 | 1.80 | 7.54 | 64.83 | 7.99 | 1.67 | 7.16 | Diam | 43 |
| $[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$[b] | 59.79 | 7.41 | 1.66 | 10.44 | 60.40 | 7.32 | 1.62 | 10.20 | Diam | 102 |
| $[Ni(Etnp_3)H_{0.74}]BPh_4$ | 67.78 | 8.50 | 1.88 | 7.89 | 66.85 | 8.83 | 1.95 | 7.66 | 1.07 | 45 |
| $[Ni(Etnp_3)(SO_2(OC_2H_5))]BF_4\cdot 0.5C_2H_5OH\cdot 0.5H_2O$ | 38.67 | 7.88 | 2.15 | 9.00 | 38.27 | 7.96 | 2.32 | 9.00 | Diam | 86 |
| $[Co(Etnp_3)Cl]BPh_4$ | 64.75 | 8.02 | 1.80 | 7.56 | 65.09 | 8.11 | 1.68 | 7.33 | 4.19 | 40 |

[a] Molar conductance of *ca.* $10^{-3}$ *M* soln. in nitroethane at 20 °C. [b] P: Calcd.: 11.01. Found: 11.26%.

---

*Author to whom correspondence should be addressed.

TABLE II. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes.

| Compound | Absorption max[a], kK ($\epsilon_M$ for soln.) |
|---|---|
| $[Ni(Etnp_3)Cl]BPh_4$ | (a) 14.5, 19.3, 25.0sh |
| | (b) 15.1(1450), 20.0(454) |
| $[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$ | (a) 21.7 |
| | (b) 21.7(2235) |
| $[Ni(Etnp_3)H_{0.74}]BPh_4$ | (a) 6.0, 7.8, 15.5, 26.0 |
| | (b) 16.3(85), 26.0(1500) |
| $[Ni(Etnp_3)(SO_2(OC_2H_5))]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ | (a) 17.9, 23.4sh |
| | (b) 17.5(4910) |
| $[Co(Etnp_3)Cl]BPh_4$ | (a) 6.2, 11.1, 13.6, 19.6, 27.8 |
| | (b) 6.4(87), 10.8(183), 13.6(358), 18.9(507) |

[a] Key: (a), solid; (b), nitromethane soln.

bound to the phosphorus atoms on the complexing properties of such tripod-like ligands.

We report the synthesis of the ligand tris(2-diethylphosphinoethyl)amine, $N(CH_2CH_2P(C_2H_5)_2)_3$, Etnp$_3$, and some of its reactions with cobalt(II) and nickel(II) salts.

All the compounds have been characterized and their physical properties studied by usual methods.

A complete X-ray structural analysis has been carried out for the compound $[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$.

## Experimental

All materials and solvents were of reagent grade quality and were used without further purification. Diethyl ether was purified by distillation over $LiAlH_4$. All operations were performed using oxygen-free solvents under inert atmosphere. The complexes were dried in a stream of dry nitrogen. The physical measurements were executed by previously described methods [7]. The analytical, magnetic and conductivity data for the complexes are reported in Table I. Table II lists the electronic spectral data.

### *Preparation of the Ligand*

$N(CH_2CH_2Cl)_3$ [8] (8.2 g, 0.04 mol) in 50 ml of diethyl ether was added dropwise to a solution of sodium diethylphosphide prepared from tetraethyldiphosphine (12.5 g, 0.07 mol) and sodium (3.2 g, 0.14 mol) in liquid ammonia (300 ml) at –78 °C [9]. A bright orange mixture developed as the trichloride was added. Ammonia was allowed to evaporate. When the reaction mixture reached room temperature, diethyl ether (200 ml) was added. The precipitated sodium chloride was filtered off and then the ether layer was distilled at atmospheric pressure to remove the solvent. The residue distilled at 170–173 °C/0.2 torr yielding *ca.* 8 g (55%) of the ligand. *Anal.* Calcd. for $C_{18}H_{42}NP_3$: C, 59.16; H, 11.59; N, 3.83; P, 25.42%. Found: C, 59.19; H, 11.98; N, 3.97; P, 25.35%.

### *Preparation of the Complexes*

*$[Ni(Etnp_3)Cl]BPh_4$ (1)*

Stoichiometric amounts of the ligand in methylene chloride (15 ml) and $NaBPh_4$ in ethanol (20 ml) were added to a solution of $NiCl_2 \cdot 6H_2O$ in ethanol (20 ml). Evaporating the solvent dark-blue crystals precipitated which were recrystallized from acetone-ethanol.

*$[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$ (2)*

To a solution of $NiCl_2 \cdot 6H_2O$ (1.5 mmol) in ethanol (20 ml), the ligand (1 mmol) in methylene chloride (15 ml) was added and then sodium tetraphenylborate (1 mmol) dissolved in ethanol (20 ml). The resulting mixture was concentrated to give orange crystals which were recrystallized from acetone-ethanol.

*$[Ni(Etnp_3)H_{0.74}]BPh_4$ (3)*

Sodium borohydride (2.5 mmol) dissolved in absolute ethanol (20 ml) was added dropwise with stirring to a boiling mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol) in ethanol (20 ml) and of the ligand (1 mmol) in acetone (40 ml). The colour of the solution changed from an intense green to orange. $NaBPh_4$ (1 mmol) was then added. The solution was concentrated by heating and golden yellow crystals quickly appeared.

*$[Ni(Etnp_3)(SO_2(OC_2H_5))]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ (4)*

The ligand (1 mmol) in methylene chloride (10 ml) was added to a solution of $Ni(BF_4)_2 \cdot 6H_2O$ (1 mmol) in ethanol (20 ml). When sulfur dioxide was bubbled into the solution, at room temperature, a deep blue color immediately appeared. The solution was slowly concentrated to give blue crystals which were recrystallized from methylene chloride-ethanol.

TABLE III.[a]

| Atom | X | Y | Z | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|---|---|---|
| NI1 | 3(1) | 2489(1) | 1594(2) | 605(15) | 696(16) | 537(14) | −70(14) | 115(11) | −135(15) |
| NI2 | 0 | 0 | 0 | 958(29) | 527(22) | 505(22) | −170(19) | 158(20) | −63(21) |
| CL1 | −924(3) | 4609(3) | 4174(4) | 1031(44) | 639(34) | 1044(43) | −163(32) | 105(37) | −121(33) |
| CL2 | 374(3) | 2721(3) | 89(4) | 886(40) | 1287(50) | 579(32) | −97(32) | 149(30) | −109(35) |
| P1 | −919(3) | 3114(4) | 1128(5) | 970(49) | 1014(50) | 864(45) | 165(38) | 109(39) | −89(39) |
| P2 | 829(3) | 1728(4) | 2084(4) | 897(47) | 1297(55) | 586(37) | 343(37) | 30(34) | −220(41) |
| P3 | 268(3) | 3809(3) | 5540(4) | 1562(60) | 503(35) | 465(33) | −195(28) | 108(37) | −61(37) |

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U11H^2A^{*2} + U22K^2B^{*2} + U33L^2C^{*2} + 2U12HKA^*B^* + 2U13HLA^*B^* + 2U23KLB^*C^*)]$ all quantities are multiplied by $10^4$.

### *[Co(Etnp$_3$)Cl]BPh$_4$ (5)*

A solution of $CoCl_2 \cdot 6H_2O$ (1 mmol) in ethanol (20 ml) was mixed with the ligand (1 mmol) in methylene chloride (10 ml). Upon addition of $NaBPh_4$ (1 mmol) in ethanol (20 ml) magenta crystals were obtained. They were recrystallized from acetone-ethanol.

### *Crystal Data and Data Collection*

A prismatic crystal with dimensions 0.42 × 0.12 × 0.08 mm along crystal axes was chosen for X-ray work. Unit cell parameters obtained and refined by using the standard routines of the Philips PW 1100 automated diffractometer are: $a$ = 20.067(5), $b$ = 17.555(5), $c$ = 12.652(4) Å, $\beta$ = 95.36(9)°. An analysis of systematic absence identified the space group as monoclinic $P2_1/n$. The density measured by flotation is in good agreement with the value calculated for two $C_{84}H_{124}N_2B_2Cl_4Ni_3P_6$ unit formulae in the cell ($D_m$ = 1.27 gcm$^{-3}$ *versus* $D_c$ = 1.26 gcm$^{-3}$). Thus the molecule must contain an inner crystallographic symmetry element in order to match such an unit formula with the general multiplicity of the space group ($Z$ = 4). The intensity data were collected by using Mo-K$\alpha$ radiation, monochromatized with a flat graphite crystal. A total of 2070 reflections with $\theta \leqslant 20°$ and with $I \geqslant 3\sigma(I)$ were considered as observed. The data collection technique was "$\omega$–$2\theta$". There was no hint of any crystal decay from the examination of three monitoring standard reflections. The data were corrected for absorption. The transmission coefficients for the crystal chosen varied between 0.95 and 0.85, as calculated by using a linear absorption coefficient of 8.6 for Mo-K$\alpha$. The data reduction as well as the structure solution and refinement were performed by using SHELX [10] and other programs locally written and implemented on a SEL 32/70 computer installed in our laboratory.

### *Structure Determination*

The structure was solved by direct methods. About half of the non-hydrogen atoms were located in the first E-Map. As expected one nickel atom lies on a center of symmetry. Subsequent Fourier maps allowed the location of the missing non-hydrogen atoms. Refinement was undertaken by means of full matrix least squares techniques; the function minimized was $\Sigma w(|F_o|-|F_c|)^2$ where $w$ is taken as $1/\sigma^2(F_o) + 0.0001\ (F_o)^2$. Initial cycles by using isotropic temperature factors for all atoms lowered the $R$ factor ($R = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$) to 0.15. The temperature factors associated with the atoms of the ethylenic chains, especially those of the terminal methyl groups, increased noticeably. This is not completely unexpected and it is probably due either to disorder or high thermal motion. However a detailed analysis of $\Delta F$ Fouriers showed double positions for at least four of the six independent terminal methyl groups. When ascertained, split positions were both introduced in subsequent least squares cycles by imposing that the sum of their population parameters, which were refined, was fixed at 1. Other types of constraints were adopted in the refinement of the ethylenic fragments such as fixed P–C distances (1.84 Å) and C–C distances (1.50 Å). Anisotropic temperature factors were introduced for Ni, P, Cl atoms. The phenyl groups were treated as rigid bodies with $D_{6h}$ symmetry (C–C distance = 1.395 Å). Hydrogen atoms were introduced at calculated positions except for ethylenic fragments. The final reliability $R$ factor is 0.079 while the weighted $R_w$ is 0.078. Final values of the atomic parameters are reported in Tables III and IV. A Table of structure factors is available from the Editor on request.

## Results and Discussion

### *Nickel Complexes*

When stoichiometric amounts of $Etnp_3$ and nickel(II) chloride in methylene chloride-alcohol are allowed to react, the colour of the solution turns deep blue. Upon addition of $NaBPh_4$ dark blue crystals of the composition $[Ni(Etnp_3)Cl]BPh_4$ (*1*) are precipitated.

TABLE IV.[a]

| Atom | X | Y | Z | U ($Å^2$) |
|---|---|---|---|---|
| N1 | −315(7) | 2333(7) | 2971(10) | 606(40) |
| C1 | −1074(8) | 2373(10) | 2957(14) | 767(57) |
| C2 | −1352(9) | 3035(10) | 2326(15) | 877(65) |
| C3 | −89(9) | 1590(10) | 3444(15) | 753(58) |
| C4 | 624(9) | 1447(10) | 3412(14) | 771(60) |
| C5 | −1(8) | 2996(8) | 3617(12) | 509(48) |
| C6 | −156(8) | 3012(9) | 4785(13) | 673(55) |
| C7 | −1452(9) | 2652(11) | 49(13) | 1238(81) |
| C8 | −1559(12) | 1814(12) | 206(21) | 1442(95) |
| C9 | −968(18) | 4049(10) | 464(24) | 2126(141) |
| C10* | −542(22) | 4513(24) | 1236(30) | 1572(233) |
| C10 | −1134(35) | 4813(21) | 880(50) | 1120(356) |
| C11 | 1698(6) | 2066(16) | 2088(22) | 1691(112) |
| C12* | 2268(16) | 2011(24) | 2928(25) | 1017(201) |
| C12 | 1914(25) | 2597(26) | 2968(29) | 1070(258) |
| C13 | 1054(13) | 974(13) | 1171(22) | 2306(148) |
| C14* | 442(13) | 537(14) | 1333(22) | 968(137) |
| C14 | 684(19) | 562(23) | 268(26) | 263(228) |
| C15 | 231(13) | 3592(16) | 6955(8) | 1825(121) |
| C16* | −491(13) | 3750(16) | 6962(25) | 912(145) |
| C16 | −62(22) | 4117(20) | 7721(29) | 470(215) |
| C17 | 1170(5) | 3600(12) | 5558(18) | 1151(80) |
| C18 | 1395(15) | 2885(14) | 6127(25) | 2103(138) |
| C19 | 2206(5) | 8114(8) | 4797(8) | 629(53) |
| C20 | 1863(5) | 7458(8) | 4441(8) | 643(49) |
| C21 | 2071(5) | 6747(8) | 4840(8) | 673(54) |
| C22 | 2622(5) | 6693(8) | 5594(8) | 781(60) |
| C23 | 2965(5) | 7349(8) | 5950(8) | 896(64) |
| C24 | 2757(5) | 8060(8) | 5551(8) | 835(62) |
| C25 | 1172(5) | −1092(6) | 3678(9) | 572(49) |
| C26 | 1030(5) | −1496(6) | 2735(9) | 667(54) |
| C27 | 373(5) | −1543(6) | 2270(9) | 768(59) |
| C28 | −142(5) | −1185(6) | 2748(9) | 785(59) |
| C29 | 0(5) | −780(6) | 3692(9) | 672(54) |
| C30 | 657(5) | −734(6) | 4156(9) | 644(53) |
| C31 | 2003(5) | −350(7) | 5175(7) | 649(53) |
| C32 | 2055(5) | 408(7) | 4858(7) | 718(57) |
| C33 | 2036(5) | 992(7) | 5602(7) | 803(60) |
| C34 | 1965(5) | 819(7) | 6661(7) | 880(64) |
| C35 | 1913(5) | 62(7) | 6978(7) | 1238(81) |
| C36 | 1932(5) | −522(7) | 6234(7) | 875(64) |
| C37 | 2501(4) | 9202(6) | 3353(10) | 537(48) |
| C38 | 2270(4) | 9499(6) | 2363(10) | 740(58) |
| C39 | 2725(4) | 9718(6) | 1651(10) | 916(66) |
| C40 | 3411(4) | 9639(6) | 1930(10) | 835(62) |
| C41 | 3642(4) | 9342(6) | 2919(10) | 1072(75) |
| C42 | 3186(4) | 9123(6) | 3631(10) | 782(60) |
| B | 1951(10) | −1032(11) | 4218(15) | 556(61) |

[a] All quantities are multiplied by $10^4$. C atoms labelled with * have refined population parameters of 0.65, 0.56, 0.68, 0.65 respectively. The sum of population parameters of C atoms labelled with the same number was constrained to 1.

If the same reaction is carried out with an excess of metal salt (metal-ligand ratio 1.5) a red solution is obtained, from which the orange complex $[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$ (*2*) is precipitated.

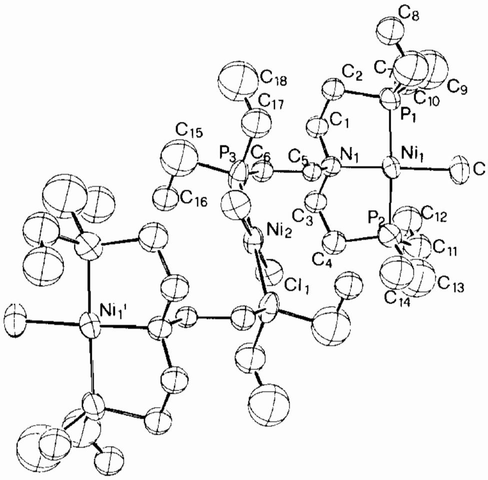


Fig. 1. The molecular structure of $[Ni_3(Etnp_3)_2Cl_4](BPh_4)_2$. For the sake of clarity only one ellipsoid is drawn for those ethylic carbon atoms found to lie on split positions.

Both compounds (*1*) and (*2*) are diamagnetic and stable in air in the solid state. They are soluble in the common organic solvents in which they behave as 1:1 and 1:2 electrolytes, respectively.

The electronic spectrum of compound (*1*), with bands at 14.5, 19.3 kK and a shoulder at 25.0 kK, is fully comparable to that of the low-spin trigonal-bipyramidal complex $[Ni(np_3)Cl]BPh_4$ [11].

The spectrum of compound (*2*), with no bands at frequencies <20 kK, is typical of the square-planar nickel(II) complexes [12].

The X-ray analysis of compound (*2*) has shown that its structure consists of tetraphenylborate anions and trinuclear $[(Ni_3(Etnp_3)_2Cl_4]^{2+}$ dications. Figure 1 shows a drawing of the complex dication.

Each nickel center is square planarly coordinated. The central one, lying on a center of symmetry, is linked to two chlorine atoms and to two phosphorus atoms from different $Etnp_3$ ligands; the other two nickel atoms, which are crystallographically equivalent, are each one coordinated by the nitrogen and the remaining phosphorus atoms of each $Etnp_3$ ligand. A chlorine atom lies on the fourth position of the square. Thus two $Etnp_3$ ligands cement together three nickel centers.

At variance with the behaviour observed for the methylated $np_3$ ligand which shared its three arms with three different metal atoms [6], the analogous ethylated ligand shares its arms with only two metal atoms by functioning as monodentate toward the first and tridentate toward the second one.

Although distortions from ideal square planar coordination are observed in all of the three units, the central square is more regular than the terminal ones. This can be probably attributed to the geometric requirements of the $Etnp_3$ ligand when it envelopes

TABLE V. Selected Bond Distances (Å) and Angles (deg.) with Their Estimated Standard Deviations.

| | |
|---|---|
| | *Bond Distances* |
| Ni(1)–Cl(2) | 2.148(5) |
| Ni(1)–P(1) | 2.184(6) |
| Ni(1)–P(2) | 2.174(6) |
| Ni(1)–N(1) | 1.929(13) |
| Ni(2)–Cl(1) | 2.153(5) |
| Ni(2)–P(3) | 2.250(5) |
| N(1)–C(1) | 1.525(18) |
| N(1)–C(3) | 1.487(18) |
| N(1)–C(5) | 1.523(17) |
| C(1)–C(2) | 1.488(20) |
| C(3)–C(4) | 1.458(19) |
| C(5)–C(6) | 1.539(20) |
| | *Bond Angles* |
| P(1)–Ni(1)–P(2) | 171.9(3) |
| P(1)–Ni(1)–Cl(2) | 91.2(2) |
| P(2)–Ni(1)–Cl(2) | 93.0(2) |
| P(1)–Ni(1)–N(1) | 88.4(4) |
| P(2)–Ni(1)–N(1) | 87.9(4) |
| N(1)–Ni(1)–Cl(2) | 176.9(4) |
| P(3)–Ni(2)–Cl(1) | 91.2(2) |
| C(1)–N(1)–C(3) | 108.1(1.3) |
| C(1)–N(1)–C(5) | 109.5(1.2) |
| C(3)–N(1)–C(5) | 111.0(1.3) |

the metal by functioning as tridentate. As one can argue by observing that the N–Ni–P angles are both smaller than 90°, the donor atoms of the ligand cannot occupy the ideal positions of the square.

Interestingly however the Ni–P bonds (2.179(6) Å) are stronger in the terminal rather than in the central square unit (2.250(5) Å) while the Ni–Cl distances are invariant (2.150(5) Å av.). Selected bond lengths and bond angles are given in Table V.

The reaction of $Etnp_3$ with nickel(II) tetrafluoroborate (or other nickel(II) salts containing low coordinating anions such as $ClO_4^-$, $NO_3^-$) turns into deep violet the colour of the solution, from which a violet solid is precipitated. Efforts to obtain crystals have failed. On the basis of spectroscopic, magnetic, and conductivity measurements, this compound may be assigned the same composition and geometry of the $Menp_3$ derivative $[Ni_3(Menp_3)_4](BF_4)_6$ [6].

A mixture of nickel(II) nitrate and $Etnp_3$ reacts with an excess of $NaBH_4$ in presence of $NaBPh_4$ in acetone-alcohol at boiling temperature to give a golden yellow crystalline product.

This compound is fairly stable in air but decomposes rapidly in 1,2-dichloroethane or nitroethane unless air is excluded in which case it behaves as 1:1 electrolyte. The compound is paramagnetic with a magnetic moment of 1.07 $\mu_B$ at room temperature. The reflectance spectrum has bands at 6.0, 7.9, 14.7 and 25.6 kK. The infrared spectrum shows two bands which can be associated with the hydride ligand at 1920 and 595 $cm^{-1}$. These values compare well with the analogous frequencies found in other five coordinate hydrido complexes of nickel with tripod ligands [13, 14]. On the basis of analytical, spectroscopic and magnetic measurements this compound is assigned the composition $[Ni(Etnp_3)H_x]BPh_4$ (*3*) where $x = 0.74$. This $x$ value is calculated from the expression $1 - x = \mu_{eff}^2/4.41$ which relates the amount of hydride with the magnetic moment of the complex [13].

Sulfur dioxide reacts with nickel(II) aquoions and the ligand $Etnp_3$ in presence of $NaBPh_4$ in ethanol-methylene chloride forming blue crystals of formula $[Ni(Etnp_3)(SO_2(OC_2H_5))]BF_4 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ (*4*).

This diamagnetic compound is stable in air, either in the solid state or in solution in polar solvents like methylene chloride or nitroethane in which it behaves as 1:1 electrolyte. The electronic reflectance spectrum with an intense band at 17.9 kK and a second weaker band above 23 kK is closely related to those of the trigonal bipyramidal nickel(II) complexes [11, 15]. The IR spectrum shows two strong bands at 1210 and 635 $cm^{-1}$ which can be attributed to the alkylsulfito group $SO_2(OC_2H_5)$ as in the analogous compounds with the $np_3$ and $PP_3$ [16] ligands.

### *Cobalt Complexes*

Cobalt(II) chloride reacts with $Etnp_3$ and $NaBPh_4$ in alcohol-methylene chloride to give magenta crystals of the composition $[Co(Etnp_3)Cl]BPh_4$ (*5*).

Compound (*5*) is stable in air and soluble in polar organic solvents in which it behaves as 1:1 electrolyte.

The room temperature magnetic moment is 4.20 $\mu_B$. The electronic spectrum has five bands at 6.2, 11.3, 13.8, 19.6 and 27.8 kK. The features of the spectrum as well as the frequencies are very similar to those found in the high-spin cobalt(II) complex $[Co(np_3)Cl]BPh_4$ with trigonal bipyramidal geometry [11].

The reaction of $Etnp_3$ with cobalt(II) tetrafluoroborate (or other cobalt(II) salts containing low coordinating anions such as $ClO_4^-$, $NO_3^-$) produces a deep-green solution from which a green solid is precipitated.

As in the case of the above reported nickel derivative, the compound may be assigned the same structure as that found by X-ray diffraction for the complex $[Co_3(Menp_3)_4](BF_4)_6$ [6].

## Conclusions

The $Etnp_3$ ligand shows a variety of behaviours which under certain circumstances make it resemble to the classical phenylated np$_3$ ligand or to the methylated Menp$_3$ ligand. A more specific behaviour has also been observed for this ethylated ligand in compounds of the type [Ni$_3$(Etnp$_3$)$_2$X$_4$]Y$_2$ whose structure has been here reported.

The dominating effect in determining the formation of the complexes seems to be the steric hindrance of the phosphorus substituents in this type of tripod ligands.

In particular the ethylated ligand, due to its large variety of behaviours, seems to be near to a crossover point. Thus depending on the reaction conditions (such as the ratio between reagents or the presence of some specific co-reagents) the formation of different types of compounds may result.

## Acknowledgements

Thanks are expressed to Mr. F. Nuzzi for microanalyses and Mr. D. Masi for technical assistance.

## References

1 C. Mealli and L. Sacconi, *Chem. Comm.*, 886 (1973).
2 P. Dapporto and L. Sacconi, *J. Chem. Soc. A*, 1804 (1970).
3 C. Mealli, P. L. Orioli and L. Sacconi, *J. Chem. Soc. A*, 2691 (1971).
4 M. Di Vaira, A. Meli and L. Sacconi, *Cryst. Struct. Comm.*, *6*, 727 (1977).
5 C. A. Ghilardi, A. Sabatini and L. Sacconi, *Inorg. Chem.*, *15*, 2763 (1976).
6 C. Bianchini, C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chim. Acta*, *31*, L433 (1978).
7 L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 2997 (1968); L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, *7*, 1417 (1968).
8 J. P. Mason and D. J. Gosch, *J. Am. Chem. Soc.*, *60*, 2816 (1938).
9 G. Kordosky, B. R. Cook, J. Cloyd Jr. and D. W. Meek, *Inorg. Synth.*, *14*, 14 (1973).
10 'SHELX-76' System of programs, G. M. Sheldrick 1976.
11 L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, *90*, 5443 (1968).
12 A. B. P. Lever, 'Inorganic Electron Spectroscopy', Elsevier, Amsterdam (1968), and references therein.
13 L. Sacconi, A. Orlandini and S. Midollini, *Inorg. Chem.*, *13*, 2850 (1974).
14 C. A. Ghilardi, S. Midollini and L. Sacconi, *Inorg. Chem.*, *14*, 1790 (1975).
15 R. B. King, R. N. Kapoor, M. S. Saran and P. N. Kapoor, *Inorg. Chem.*, *10*, 1851 (1971).
16 C. A. Ghilardi, S. Midollini and L. Sacconi, *Inorg. Chem.*, *16*, 2377 (1977).