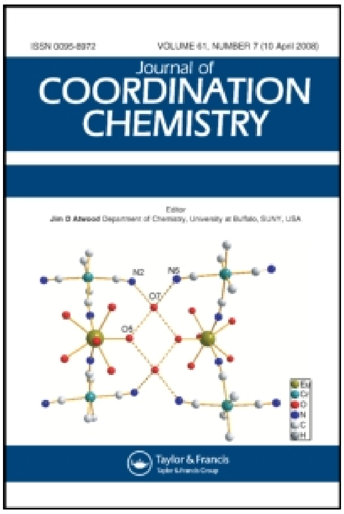

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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES OF MONO- AND DINUCLEAR COMPLEXES OF NICKEL(II) AND COBALT(II) WITH HEXADENTATE LIGANDS HAVING N_2P_4 DONOR ATOMS. CRYSTAL STRUCTURE OF $[Ni(BDPE)](ClO_4)_2 \cdot CH_2Cl_2$

Parimal Paul[a]; K. Venkatasubramanian[a]; Sapna Purohit[a]
[a] Discipline of Coordination Chemistry and Homogeneous Catalysis, Central Salt and Marine Chemicals Research Institute, Bhavnagar, India

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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES OF MONO- AND DINUCLEAR COMPLEXES OF NICKEL(II) AND COBALT(II) WITH HEXADENTATE LIGANDS HAVING N_2P_4 DONOR ATOMS. CRYSTAL STRUCTURE OF $[Ni(BDPE)]ClO_4)_2.CH_2Cl_2$

PARIMAL PAUL, K. VENKATASUBRAMANIAN* and SAPNA PUROHIT

Discipline of Coordination Chemistry and Homogeneous Catalysis, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

(Received July 8, 1992)

A series of mono- and dinuclear complexes of Ni(II) and Co(II) with two hexadentate ligands α,α'-bis(bis(2-(diphenylphosphino)ethyl)amino)ethane (BDPE) and α,α'-bis(bis(2-(diphenylphosphino)ethyl)-amino)-*m*-xylene (BDPX) were synthesized and chracterized by means of elemental analyses, molar conductance, magnetic susceptibilities, infrared, electronic and ^{31}P NMR data. The molecular structure of a mononuclear Ni(II) complex, $[Ni(BDPE)](ClO_4)_2.CH_2Cl_2$, was established by single-crystal X-ray diffraction methods. Crystal data: $C_{59}H_{62}NiCl_4N_2O_8P_4$, $M=1250.98$, orthorhombic, space group *Pbca*, $V=11834.3(7)$ Å3, $Z=8$, $a=10.817(1)$, $b=31.683(7)$, $c=34.538(1)$ Å, final R 0.055 ($R_w=0.057$) for 3118 observed reflections. The Ni(II) ion exists in a slightly distorted square planar geometry, the coordination sites being two phosphorous and two tertiary nitrogen atoms of the ligand. Electrochemical studies of the complexes were also carried out.

KEY WORDS: Polyphosphine, nickel, cobalt, electrochemistry, X-ray structure.

INTRODUCTION

The synthesis and characterization of transition metal complexes with chelated tertiary phosphine ligands has gained considerable importance due to their interesting structural chemistry[1–10] and catalytic activity.[11–14] A number of such complexes with bidentate,[15] terdentate,[16–18] tetradentate[19] and hexadentate[20–23] ligands with phosphorus or nitrogen and phosphorus donor atoms have been reported from this laboratory[15–20] as well as by others.[21–23] Among these the chemistry of hexadentate ligands is less extensive, and is mainly restricted to hexaphosphine ligand systems, except for one ligand[20] which has N_2P_4 donor atoms. The chemistry of such a polydentate mixed donor system is interesting because it contains both σ-donor and π-aceptor coordinating atoms as a result of which it is capable of controlling electron density on a metal ion, as is important in homogeneous catalysis; in addition it can form mono- as well as multinuclear complexes which are structurally interesting.

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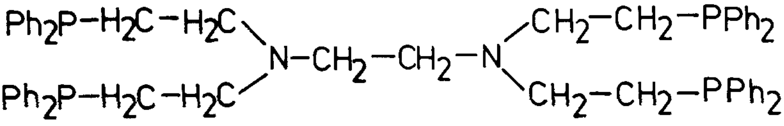
* Author for correspondence.



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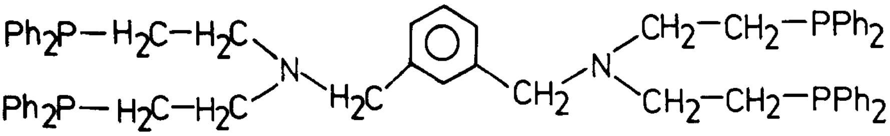

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In this particular system we have synthesized two hexadentate ligands, *viz* α,α′-bis(bis(2-(diphenylphosphino)ethyl)amino)ethane (BDPE) (Structure **1**) and α,α′-α,α′-bis(bis(2-(diphenylphosphino)ethyl)amino)-*m*-xylene (BDPX) (Structure **2**) which have N_2P_4 donor atoms. These ligands are bifunctional, i.e., can form mono- as well as dinuclear complexes. This paper reports the synthesis, characterization and electrochemical studies of mono- and dinuclear complexes of Ni(II) and Co(II) with the same ligands. Structural characterization of $[Ni(BDPE)](ClO_4)_2.CH_2Cl_2$ is also reported.

EXPERIMENTAL

Materials

The ligands BDPE and BDPX were prepared by reported methods.[24] Sodium tetraphenylborate, $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$ were obtained from Aldrich Chemical Co. $Ni(ClO_4).6H_2O$ and $Co(ClO_4)_2.6H_2O$ were prepared by the reaction of perchloric acid with the corresponding carbonate.

All organic solvents used were of reagent grade and were purified and dried by standard procedures. All preparations were carried out under dry nitrogen or argon.

Physical Measurements

C, H and N analyses were performed using a Carlo Erba 1106 instrument. A Digisun Electronics digital conductivity meter (model D1-909) was used for conductivity measurements. Magnetic measurements were carried out with a PAR 115 vibrting sample magnetometer. Infrared spectra were recorded on a Carl Zeiss Specord M80 spectrometer, in KBr pellets or nujol mulls. ^{31}P NMR spectra were recorded on a Jeol FX-100 FT NMR operating at 40.27 MHz in the indicated solvents using a capillary of deuterium oxide for the internal lock and 85% H_3PO_4 as external standard. Electronic spectra were recorded on a Shimadzu UV-160 spectrometer. Electrochemical measurements were made with a Princeton Applied Research electrochemical instrument equipped with a precision X-Y recorder. A PAR 174A polarographic analyzer was used to record dc and differential pulse polarograms; a PAR 175 universal programme coupled with the PAR 174A analyzer was used for recording cyclic voltammograms. A PAR 303 SMDE assembly provided with a DME/HMDE working electrode and platinum wire (0.5 mm diameter) was used. All potentials were measured against an Ag/AgCl reference electrode at 25 ± 1°C. Tetrabutylammonium perchlorate was used as supporting electrolyte. A medium sized drop (2.75 mg mass) was used with an open circuit and a 2 s drop time. Cyclic voltammetry was performed with scan rates from 100 to 500 mV/s.

Synthesis of Metal Complexes

$[Ni_2(BDPE)Cl_2](BPh_4)_2$ (1)

To an ethanolic solution (25 cm^3) of $NiCl_2.6H_2O$ (0.119 g, 0.5 mmol), BDPE ligand (0.227 g, 0.25 mmol) dissolved in dichloromethane (5 cm^3) was added dropwise with stirring at room temperature. Stirring was continued for 2 h. To the clear solution an ethanolic solution of $NaBPh_4$ (0.21 g, 0.6 mmol) was added slowly. the reddish-brown compound which separated was collected by filtration, washed with water and ethanol and recrystallized from dichloromethane-ethanol yield 0.37 g (85%).

$[Ni_2(BDPX)Cl_2](BPh_4)_2$ (2)

This compound was synthesized following the same procedure as described for (1), colour reddish-brown, yield 0.35 g (78%).

$[Ni(BDPE)](ClO_4)_2.CH_2Cl_2$ (3)

BDPE (0.454 g, 0.5 mmol) was suspended in methanol (50 cm^3) and a methanolic solution (15 cm^3) of $Ni(ClO_4)_2.6H_2O$ (0.183 g, 0.5 mmol) was added slowly with stirring at room temperature. Stirring was continued for 2 h during which a yellow compound separated. The compound was isolated by filtration, washed with benzene and methanol and recrystallized from dichloromethane-ethanol, yield 0.54 g (87%).

$[Ni_2(BDPX)(H_2O)_2)](ClO_4)_4$(4) and $[Ni(BDPX)](ClO_4)_2$ (5)

The same procedure as described for compound (3) is followed for the preparation of (4) and (5) except a 1:2 molar ratio of BDPX and $Ni(ClO_4)_2.6H_2O$ was employed. The compounds were not precipitated during stirring. The volume of the solution was reduced to *ca* 5 cm^3, diethyl ether (5 cm^3) was added dropwise and he mixture was kept in the refrigerator for 24 h. A brown compound separated, and which on recrystallization from methanol-ether mixture twice, resulted in the pure compound (4). Yield 0.36 g. The filtrate was dried on a rotary evaporator and the residue washed with benzene and ether. Recrystallization from chloroform-ethanol gave (5), yield 0.16 g.

$[Co_2(BDPE)Cl_2])BPh_4)_2$ (6) and $[Co_2(BDPX)Cl_2](BPh_4)_2$ (7)

Compounds (6) and (7) were synthesized by the reaction of BDPE and BDPX with $CoCl_2.6H_2O$ following the same procedure as described for (1). Yields 0.32 g (74%) for (6) and 0.31 g (68%) for (7).

Table 1 Elemental analysis, magnetic susceptibility and conducivity data for the complexes

Complex	Analytical data %C	%H	%N	μ_{eff} (B.M.)	Molar conductance Solvent	$\Lambda_M(\Omega^{-1}\ cm^2\ mol^{-1})$
$[Ni_2(BDPE)Cl_2](BPh_4)_2$ (1)	72.87 (73.34)	5.62 (5.77)	1.54 (1.61)	diamagnetic	$NCCH_3$	228[a]
$[Ni_2(BDPX)Cl_2](BPh_4)_2$ (2)	73.89 (7424)	5.87 (5.74)	1.42 (1.55)	diamagnetic	$NCCH_3$	244[a]
$[Ni(BDPE)](ClO_4)_2.CH_2Cl_2$ (3(	56.48 (56.61)	5.08 (4.96)	2.11 (2.24)	diamagnetic	$NCCH_3$	238[a]
$[Ni_2(BDPX)(H_2O)_2](ClO_4)_4$ (4)	49.68 (50.02)	4.58 (4.43)	1.70 (1.82)	diamagnetic	DMF	295[b]
$[Ni(BDPX)](ClO_4)_2$ (5)	61.64 (61.85)	5.21 (5.15)	2.17 (2.25)	diamagnetic	$NCCH_3$	242[a]
$[Co_2(BDPE)Cl_2](BPh_4)_2$ (6)	72.95 (73.31)	5.76 (5.88)	1.61 (1.50)	4.41[d]	$NCCH_3$	256[a]
$[Co_2(BPDX)Cl_2](BPh_4)_2$ (7)	73.93 (74.21)	5.69 (5.74)	1.48 (1.55)	4.38[d]	$NCCH_3$	245[a]
$[Co(BDPE)](BPh_4)_2$ (8)	78.87 (79.25)	6.36 (6.23)	1.65 (1.74)	4.32	$NCCH_3$	230[a]
$[Co_2(BDPE)Cl_4]$ (9)	59.73 (59.59)	5.26 (5.14)	2.32 (2.40)	4.42[d]	DMF	12[c]
$[Co_2(BDPX)Cl_4]$ (10)	61.58 (61.74)	5.20 (5.14)	2.14 (2.25)	4.46[d]	DMF	10[c]
$[Co(BDPE)](ClO_4)_2$ (11)	59.48 (59.69)	5.13 (5.15)	2.21 (2.40)	4.22	DMF	140[a]
$[Co(BDPX)](ClO_4)_2$ (12)	61.78 (61.84)	5.26 (5.15)	2.14 (2.25)	4.36	DMF	136[a]

[a] 1:2 electrolyte.
[b] 1:4 electrolyte.
[c] nonelectrolyte.
[d] μ_{eff} per cobalt ion.

Table 2 Selected IR bands and $^{31}P\{^1H\}$ NMR data for the complexes

Complex	IR bands (cm^{-1})[a] $\nu(M—P)$	$\nu(M—Cl)$	Others	$^{31}P\{^1H\}$ NMR data Solvent	Chemical shift, δ
$[Ni_2(BDPE)Cl_2](BPh_4)_2$ (1)	512	354		MeOH	35.12
$[Ni_2(BDPX)Cl_2](BPh_4)_2$ (2)	510	355		MeOH	35.00
$[Ni(BDPE)](ClO_4)_2.CH_2Cl_2$ (3)	510		1100, 625[b]	CH_2Cl_2	32.27, −19.05
$[Ni_2(BDPX)(H_2O)_2](ClO_4)_4$ (4)[c]	515		1100, 625b	MeOH	35.42
$[Ni(BDPX)](ClO_4)_2$ (5)	508		1100, 625[b]	MeOH	31.62, −20.89
$[Co_2(BDPE)Cl_2](BPh_4)_2$ (6)	470	302		MeOH	36.04
$[Co_2(BDPX)Cl_2](BPh_4)_2$ (7)	472	305		MeOH	37.2
$[Co(BDPE)](BPh_4)_2$ (8)	470			CH_2Cl_2	34.88, −20.04
$[Co_2(BDPE)Cl_4]$ (9)	472	308		CH_2Cl_2	38.94
$[Co_2(BDPX)Cl_4]$ (10)	470	310		Ch_2Cl_2	39.04
$[Co(BDPE)](ClO_4)_2$ (11)	478		1100, 625[b]	MeOH	34.82, −20.22
$[Co(BDPX)](ClO_4)_2$ (12)	474		1100, 625[b]	MeOH	35.54, −20.46

[a] In KBr.
[b] Due to ClO_4^-.
[c] Coordinated H_2O shows bands at 3400(br), 1630, 800 and 640 cm^{-1} (see text for assignment).

[Co(BDPE)](BPh$_4$)$_2$ (8)
BDPE (0.227 g, 0.25 mmol) suspended in methanol (25 cm^3) was added slowly with stirring to a solution containing an equimolar amount of $Co(ClO_4)_2.6H_2O$ at room temperature. After 5 h an ethanolic solution of $NaBPh_4$ (0.34 g, 0.7 mmol) was added dropwise. The green compound that separated was collected and recrystallized from DMF-ethanol (1:10), yield 0.31 g (77%).

[Co$_2$(BDPE)Cl$_4$] (9)
$CoCl_2.6H_2O$ (0.119 g, 0.5 mmol) was dissolved in the minimum volume of hot ethanol (20 cm^3) and BDPE -.0227 g, 0.25 mmol) dissolved in dichloromethane (30 cm^3) was added dropwise. The reaction mixture was refluxed for 4 h. The solvent was then removed and the solid mass extracted by dichloromethane. The volume of the dichloromethane solution was reduced to *ca* 5 cm^3. The addition of *n*-hexane separated a sky blue compound which was collected by filtration and dried *in vacuo*, yield 0.26 g (90%).

[Co$_2$(BDPX)Cl$_4$] (10)
This compound was prepared by reaction of BDPX and $CoCl_2.6H_2O$ following the same procedure as described for (9), yield 0.25 g (82%).

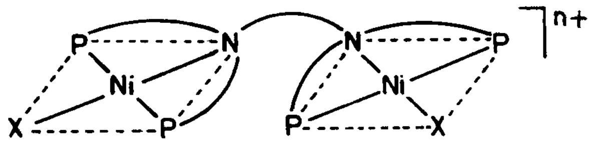
[Co(BDPE)](ClO$_4$)$_2$ (11) and [Co(BPDX)](ClO$_4$)$_2$ (12)
Compoinds (11) and (12) were synthesized by reaction of the respective ligand with $Co(ClO_4)_2.6H_2O$ following the same procedure as described for (3) and recrystallized from DMF-methanol (1:10) as shining, dark green microcrystals, yields 0.22 g (75%) for (11) and 0.21 g (68%) for (12).

X-ray Structure Determination

Preliminary data on space group and unit cell dimensions as well as intensity data were collected using a crystal of suitable size on an enraf-Nonius CAD4/PDP-11/73 system with graphite-monocromatized CuK_α radiation in the 2θ range 2–65°. Accurate unit cell dimensions were obtained using 25 arbitrarily chosen higher order reflections (θ from 28 to 30°). After correction for Lorentz and polarization factors, the intensities were corrected for absorption by an empirical absorption correction method[25] with three reflections near Chi = 90°. The structures were solved by direct methods using MULTAN, which gave the positions of the metal and phosphorus atoms unambiguously, and alternating least-squares refinement and difference Fourier maps. Hydrogen atoms for the phenyl rings and methylene groups were generated. Anisotropic refinement of non-hydrogen atoms by block-diagonal matrix methods using two blocks, with hydrogens held fixed by stereochemical constraints or in positions indicated in the difference maps, with a unit weighting scheme and Dunitz-Seiler factor[26] resulted in convergence. Scattering factors for Ni, Cl, P, oxygen, carbon and nitrogen were taken from volume IV of International tables for Crystallography[27] while those for hydrogens were from Stewart *et al.*[28] All computations were carried out using the SDP package of the Enraf-Nonius system on a PDP-11/73.[29] At the end of the refiniement, the maximum shift to error ratio was less than 0.10.

RESULTS AND DISCUSSION

Reaction of $NiCl_2.6H_2O$ with BDPE and BDPX at a 2:1 mole ratio followed by addition of NaBPh resulted in the formation of the compounds $[Ni_2(BDPE)Cl_2](BPh_4)_2$ (1) and $[Ni_2(BDPX)Cl_2](BPh_4)_2$ (2), respectively. For both compounds satisfactory elemental analysis were obtained. The complexes are diamagnetic and their conductivity data correspond to 1:2 electrolytes in acetonitrile. Infrared spectra exhibit bands at 512 and 354 cm^{-1} for (1) and 510 and 355 cm^{-1} for (2). The higher frequency band is assigned to ν(Ni—P)[18] and the other to ν(Ni—Cl).[1,15,18] $^{31}P\{^1H\}$ NMR spectra exhibit a sharp singlet at 35.12 ppm for (1) and at 35.00 ppm for (2), indicating the equivalence of phosphorus atoms coordinated to Ni(II).[6,15,18] The above data can be explained by considering the complexes to be dinuclear with square planar geometry, in which Ni(II) possesses an NPPCl core with phosphorus atoms *trans* to each other, as shown in **3**. The square planar geometry is also supported by electronic spectra which shows a strong band at 205000 cm^{-1} (ϵ, 275 M^{-1} cm^{-1}) for (1) and at 20000 cm^{-1} (ϵ, 300 M^{-1} cm^{-1}) for (2) due to the $^1A_{2g} \rightarrow {}^1A_{1g}$ transition.[15,18]



X = Cl 1 (BDPE)
2 (BDPX)
X = H_2O 4 (BDPX)

3

When $Ni(ClO_4)_2.6H_2O$ was reacted with BDPE (1:1 mole ratio) in methanol, a yellow compound, $[Ni(BDPE)](ClO_4)_2$ (3), was obtained. After recrystallization from dichloromethane-ethanol, elemental analysis showed the presence of a dichloromethane molecule in the compound. The compound is diamagnetic and conductivity data corresponds to a 1:2 electrolyte in acetonitrile. Infrared spectra of 3 showed ν(Ni—P) at 510 cm^{-1}. The presence of ClO_4^- is indicated by a broad band at 1100 cm^{-1} (ν_3) and a sharp band at 625 cm^{-1} (ν_4).[30] The $^{31}P\{^1H\}$ NMR spectrum exhibits two singlets at 32.27 ppm and −19.05 ppm with almost equal intensities, thus indicating the presence of both coordinated and free PPh_2 groups. The electronic spectrum of the complex shows a strong band at 22200 cm^{-1} (ϵ, 360 M^{-1} cm^{-1}) which may be assigned to the $^1A_{2g} \rightarrow {}^1A_{1g}$ transition of a square planar Ni(II) complex. The above data are, therefore, consistent with square planar geometry for (3) in which two nitrogen atoms and two phosphorus atoms are involved in coordination and two PPh_2 groups are free. The geometry is confirmed by the single crystal X-ray studies.

In the case of the reaction of BDPX with $Ni(ClO_4)_2.6H_2O$ at a 1:1 mole ratio a pure product could not be isolated. On conducting the same reaction at a 1:2 mole ratio, and by fractional crytallization, two pure compounds, $[Ni_2(BDPX)(H_2O)_2](ClO_4)_4$

(4) and [Ni(BDPX)]$(ClO_4)_2$ (5), were obtained as major and minor products, respectively. Both compounds are diamagnetic, the conductivity measurement showing that ClO_4^- is not involved in coordination to the metal ion.

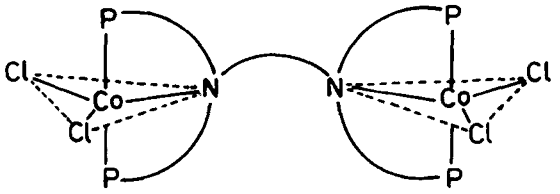
The infrared spectrum of (4) exhibits absorptions at 515 cm^{-1}, assigned to ν(Ni—P),[18] and at 1100 (broad) and 625 cm^{-1}, characteristic of uncordinated ClO_4^-. The ligation of H_2O to Ni(II) is indicated by a broad band, ν_{as} and ν_s (O—-H) centred at 3400 cm^{-1}, and a medium intensity band at 1630 cm^{-1} for H—O—H bending, a sharp band at 640 cm^{-1} for ν(Ni—O), and a strong band at 800 cm^{-1} for the wagging mode of coordinated H_2O.[31] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 35.42 ppm. The electronic spectrum has a maximum 21,200 cm^{-1} (ϵ, 130 M^{-1} $^{cm-1}$), similar to complex (2). These data are a dinuclear square planar geometry for the complex as shown in **3**.

The $^{31}P\{^1H\}$ NMR spectrum of (5) shows two sharp singlets at 31.62 and −20.89 ppm, indicating the presence of both coordinated and free PPh_2 groups. Infrared measurements show (Ni—P) at 508 cm^{-1}. The electronic spectrum has a strong band at 22200 cm^{-1} (ϵ, 280 M^{-1} $^{cm-1}$) similar to (3). These results suggest a square planar geometry for (5) as found for (3).

Reactions of BDPE and BDPX with $CoCl_2.6H_2O$ (1:2 mole ratio) in methanol followed by addition of $NaBPh_4$ resulted in the formation of $[Co_2(BDPE)Cl_2](BPh_4)_2$ (6) and $[Co_2(BDPX)Cl_2](BPh_4)_2$ (7), respectively. Both compounds behave as 1:2 electrolytes in acetonitrile. The infrared spectra of the complexes exhibit bands at 470 and 300 cm^{-1} for (6) and 472 and 305 cm^{-1} for (7), of which the higher frequency band is assigned to ν(Co-P) whereas the lower frequency band may be due to ν(Co-Cl).[1,2,18] $^{31}P\{^1H\}$ NMR spectra of (6) and (7) exhibit single peak at 36.04 and 37.24 ppm, respectively, indicating the equivalence of phosphorus atoms coordinated to Co(II) in each complex. Both compounds are paramagnetic with μ_{eff} 4.41 B.M. for (6) and 4.38 B.M. for (7), per Co(II) ion. These values are typical of tetrahedral Co(II).[32,33] Electronic spectra exhibit a single strong band in the visible region at 15600 cm^{-1} (ϵ, 220 M^{-1} $^{cm-1}$) for (6) and 15100 cm^{-1} (ϵ, 220 M^{-1} $^{cm-1}$) for (7), assigned to the $^4A_2(F)\rightarrow{}^4T_{1(P)}$ (ν_3) transition, consistent with a tetrahedral geometry for cobalt.[18,32,34] The appearance of weak shoulders on this band may be due to splitting of the $^4T_{1(P)}$ state by spin-orbit coupling[32,35] and indicates considerable deviation from Td symmetry. These data suggest a dinuclear tetrahedral structure for (6) and (7) with an NPPCl donor set around each Co(II).

Reaction of $CoCl_2.6H_2O$ with BDPE at a 1:1 mole ratio in methanol followed by addition of $NaBPh_4$ and recrystallization from DMF-MeOH gave a shining dark green microcrystalline compound. Elemental analysis confirms the composition $[Co(BDPE)](BPh_4)_2$ (8). The $^{31}P\{^1H\}$ NMR spectrum of (8) exhibits two singlets at 34.88 and −20.04 ppm indicating the presence of both ligated and free PPh_2 groups. The infrared spectrum shows ν(Co-P) at 474 cm^{-1}. The μ_{eff} of the compound is 4.32 B.M. (corresponding to 3 unpaired spins). Electronic spectra show a band at 15000 cm^{-1} (ϵ, 245 M^{-1} $^{cm-1}$), assigned to $^4A_{2(F)}\rightarrow{}^4T_{1(P)}$ (ν_3), consistent with tetrahedral Co(II) as found for (6) and (7).

Change of solvent from methanol to ethanol-dichloromethane (1:15) in the reaction of $CoCl_2.6H_2O$ with BDPE and BDPX (2:1 mole ratio) gave sky blue compounds of composition $Co_2(BPDE)Cl_4$ (9) and $Co_2(BDPX)Cl_4$ (10). Both the compounds are non-electrolytes, indicating the coordination of all four chloride ions to Co(II). $^{31}P\{^1H\}$ NMR spectra show broad peaks at 38.94 ppm for (9) and 39.04 ppm for (10), indicating tht the phosphorus atoms are equivalent and ligated to Co(II). Infrared spectra exhibit bands due to ν(Co—P) at 474 and 470 cm^{-1} and to ν(Co—Cl) at 308 and 310 cm^{-1} for (9) and (10), respectively. The compounds are paramagnetic and have μ_{eff} values of 4.42 B.M. for (9) and 4.46 B.M. for (10), per Co(II). From the above data two possible geometries can be proposed; (i) a non-bridged tetrahedral dinuclear compound in which each Co(II) ion has PPClCl coordination sites with phosphorus atoms in a *cis* disposition, and (ii) a high spin pentacoordinated dinuclear compound having a NPPClCl core for each Co(II), as shown in **4**. The electronic spectra exhibit three distinct bands in the visible region at 9200 (ϵ, 52 M^{-1} $^{cm^{-1}}$), 14300 (ϵ, 320 M^{-1} $^{cm^{-1}}$) and 17000 cm^{-1} (ϵ, 440 M^{-1} $^{cm^{-1}}$) for (9) and at 9100 (ϵ 58 M^{-1} $^{cm^{-1}}$), 14100 (ϵ, 342 M^{-1} $^{cm^{-1}}$) and 16800 cm^{-1} (ϵ, 468 M^{-1} $^{cm^{-1}}$) for (10). these data are completely different from those of the tetrahedral dinuclear complexes (6) and (7), but are very similar to reported data for high spin pentacoordinated Co(II) complexes with trigonal bipyramidal geometry.[36,37]



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$Co(ClO_4)_2.6H_2O$ reacted with BDPE and BDPX at a 1:1 mole ratio and gave dark green microcrystalline compounds of composition $[Co(BDPE)](ClO_4)_2$ (11) and $[Co(BDPX)](ClO_4)_2$ (12). They behave as 1:2 electrolytes in DMF and have magnetic moments (μ_{eff}) of 4.22 and 4.36 B.M. (for (11) and (12), respectively). $^{31}P\{^1H\}$ NMR and electronic spectra of both the compounds are similar to those of complex (8). The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at 34.82 and −20.22 ppm for (11) and 35.54 and −20.46 ppm for (12) indicating the presence of both ligated and free PPh_2 groups. Electronic spectra exhibit bsnds at 15175 cm^{-1} (ϵ, 326 M^{-1} $^{cm^{-1}}$) for (11) and at 15400 cm^{-1} (ϵ, 300 M^{-1} $^{cm^{-1}}$) for (12) with shoulders (not well resolved) on the lower energy side. Infrared spectra show characreristic bands for ClO_4^- at 1100 cm^{-1} and 625 cm^{-1} and ν(Co—P) at 478 and 474 cm^{-1} for (11) and (12), respectively. All the data are consistent with a tetrahedral geometry for both the compounds in which two nitrogen atoms and two PPh_2 groups are involved in coordination.

Structure of Complex 3

The X-ray crystal structure of complex (3) consists of discrete cations, anions and solvent molecules (CH_2Cl_2) with eight molecules in the uhit cell. An ORTEP view of the cation is shown in Fig. 1 along with the atom numbering scheme. The contents of the unit cell are shown in Fig. 2. A summary of crystal refinement data is given in Table 3. Final positional parameters are listed in Table 4; selected bond distances and angles are presented in Table 5.

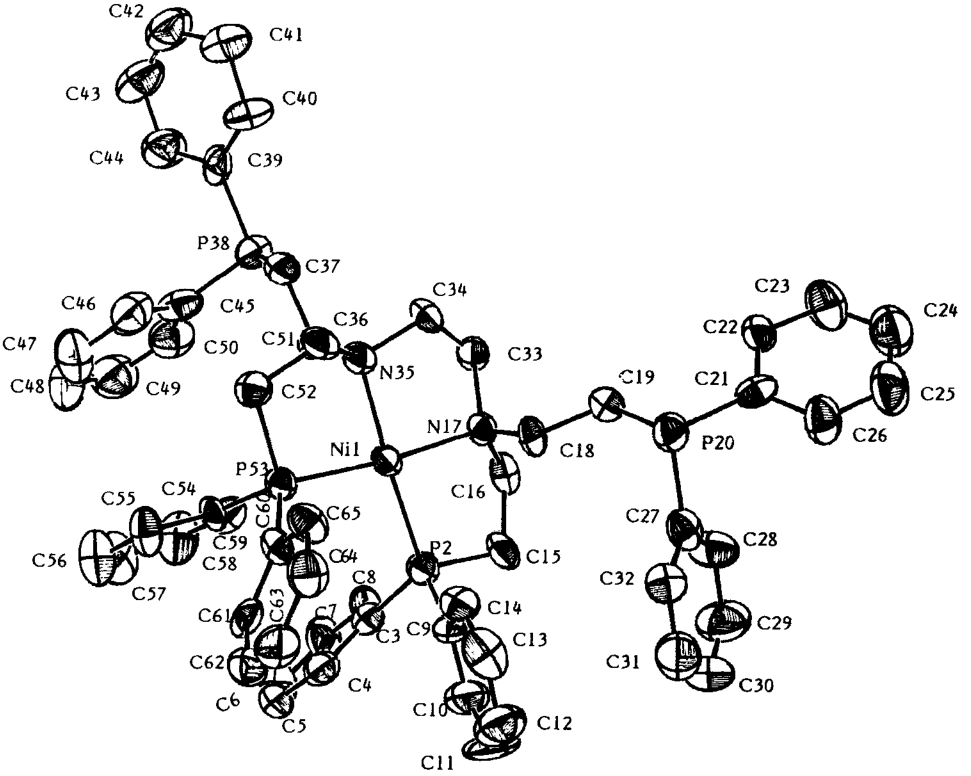

Figure 1 ORTEP diagram of the cationic part of complex (3), $[Ni(BDPE)]^{2+}$, showing the atom labeling scheme.

The structure of the cationic part of (3) shows a mononuclear nickel complex in which two of the four phosphorus atoms of PPh_2 groups and two tertiary nitrogen atoms of the ligand are coordinated to Ni(II) with a slightly distorted square planar geometry. In the coorindation sphere the displaceent of the atoms P2, P53, N35, N17 and Ni1 from the plane defined by them are 0.099(3), −0.104(3), 0.122(8), −0.125(8) and 0.008(2), respectively. The dihedral angles are: Ni1—P2—P53/Ni1—P2—N17 = 6.50(5)°, Ni1—P2—P53/Ni1—N17—N35 = 8.63(5)° and Ni1—P2—P53/Ni1—N35—P35 = 5.46(6)°. This distortion in the coordination sphere is due to the unequal sizes of the coordinating atoms (N and P) and steric crowding of the pnehyl rings of two adjacent PPh_2 groups coordinated to Ni(II).

The Ni—P bond lengths of 2.183(3) and 2.191(3)Å (Table 5) are comparable to other reported values [38,39] for square pyramidal Ni(II) complexes with an NNPP core (tetriary amine nitrogen and P atom of PPh_2) in the basal plane of the cooridnation sphere. The Ni—N distances of 1.989(7) and 1.974(7)Å also compare very well to those of other Ni(II) compounds.[38,39] The phenyl rings are planar.

A view of the molecular packing projected down the *c* axis is shown in Fig. 2. an inspection of the packing shows that the perchlorates are wedged between the cations and are not involved in H—bonding. The oxygens of two perchlorates have 18

Table 3 Summary of crystallographic data for complex (3)

Empirical formula	$C_{59}H_{62}NiN_2Cl_4O_8P_4$
Formula weight	1250.98
Space group	*Pbca* (orthorhombic)
a(Å)	10.817(1)
b(Å)	31.683(7)
c(Å)	34.538(1)
V(Å^3)	11834.3(7)
Z	8
D_{calc} (g/cm^3)	1.310
Crystal dimensions (mm)	0.27 × 0.32 × 0.22
μ (cm^{-1})	27.792
Radiation (λ, Å)	CuK$_\alpha$ (1.54184)
Temperature (°C)	25 ± 1
Total reflections	7439
Reflections used in refinement [$I > 3\sigma(I)$]	3118
R	0.055
R_w	0.057

Table 4 Positional parameters and estimate standard deviations for complex (3) for the non-hydrogen atoms

Atom	x/a	y/b	z/c	B(Å^2)
Ni1	0.0642(2)	0.12329(5)	0.64405(4)	2.82(3)
Cl66	0.4696(3)	0.33185(9)	0.91623(8)	5.77(8)
Cl71	0.5166(3)	0.1079(1)	0.66972(9)	6.33(9)
Cl76	0.3472(5)	0.0755(1)	0.0640(2)	11.4(2)
Cl77	0.1227(5)	0.0287(1)	0.0563(2)	11.8(2)
P2	0.0738(3)	0.07233(8)	0.60163(7)	3.24(6)
P20	−0.1900(3)	0.00145(9)	0.72702(8)	3.71(7)
P38	0.3854(3)	0.23850(9)	0.71344(8)	4.16(7)
P53	0.0152(3)	0.17605(8)	0.60601(7)	2.94(6)
O67	0.547(1)	0.3163(3)	0.8871(3)	11.5(4)
O68	0.450(1)	0.1310(4)	0.6431(3)	12.2(4)
O69	0.437(1)	0.3726(3)	0.9072(3)	12.6(4)
O70	0.632(1)	0.1264(5)	0.6768(3)	15.4(5)
O72	0.4497(8)	0.1046(3)	0.7045(2)	6.8(2)
O73	0.373(1)	0.3041(5)	0.9174(4)	15.3(5)
O74	0.527(1)	0.3313(3)	0.9523(3)	10.0(3)
O75	0.526(1)	0.0681(4)	0.6543(4)	15.1(5)
N17	0.0878(7)	0.0791(2)	0.6843(2)	2.8(2)
N35	0.0768(7)	0.1660(2)	0.6855(2)	3.2(2)
C3	0.1767(9)	0.0798(3)	0.5619(3)	3.0(2)
C4	0.136(1)	0.0935(3)	0.5259(3)	3.8(3)
C5	0.219(1)	0.1028(3)	0.4962(3)	4.6(3)
C6	0.343(1)	0.0971(4)	0.5016(3)	5.6(3)
C7	0.385(1)	0.0833(4)	0.5362(4)	5.7(3)
C8	0.305(1)	0.0754(3)	0.5667(3)	4.6(3)
C9	−0.068(1)	0.0520(3)	0.5806(3)	3.4(2)
C10	−0.061(1)	0.0227(3)	0.5521(3)	5.1(3)
C11	−0.168(1)	0.0059(4)	0.5368(3)	6.2(4)
C12	−0.280(1)	0.0180(4)	0.5504(4)	6.0(4)
C13	−0.290(1)	0.0463(4)	0.5801(3)	5.0(3)
C14	−0.181(1)	0.0634(3)	0.5955(3)	3.5(3)
C15	0.135(1)	0.0290(3)	0.6314(3)	4.2(3)
C16	0.177(1)	0.0469(3)	0.6700(3)	4.1(3)

Table 4 *continued*

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
C18	−0.0364(9)	0.0595(3)	0.6921(3)	3.1(2)
C19	−0.039(1)	0.0293(3)	0.7259(3)	4.0(3)
C21	−0.1697(9)	−0.0347(3)	0.7682(3)	3.3(2)
C22	−0.091(1)	−0.0278(3)	0.7988(3)	3.9(3)
C23	−0.091(1)	−0.0559(4)	0.8300(3)	5.7(3)
C24	−0.171(1)	−0.0894(4)	0.8316(3)	6.4(4)
C25	−0.249(1)	−0.0951(4)	0.8015(3)	6.0(4)
C26	−0.253(1)	−0.0686(3)	0.7697(3)	4.7(3)
C27	−0.1705(9)	−0.0351(3)	0.6868(3)	3.7(3)
C28	−0.081(1)	−0.0658(4)	0.6854(3)	5.4(3)
C29	−0.072(1)	−0.0933(4)	0.6541(4)	6.9(4)
C30	−0.156(1)	−0.0913(4)	0.6249(3)	6.9(4)
C31	−0.242(1)	−0.0596(4)	0.6256(3)	6.2(4)
C32	−0.251(1)	−0.0317(3)	0.6565(3)	5.1(3)
C33	0.137(1)	0.1017(3)	0.7187(3)	3.6(3)
C34	0.068(1)	0.1428(3)	0.7232(3)	3.7(2)
C36	0.2013(9)	0.1874(3)	0.6828(3)	3.4(3)
C37	0.219(1)	0.2242(3)	0.7106(3)	4.1(3)
C39	0.380(1)	0.2845(3)	0.7463(3)	3.8(3)
C40	0.301(1)	0.2858(3)	0.7774(3)	5.2(3)
C41	0.309(1)	0.3175(4)	0.8049(3)	6.7(4)
C42	0.393(1)	0.3492(4)	0.8000(4)	7.2(4)
C43	0.471(1)	0.3479(4)	0.7690(4)	6.6(4)
C44	0.466(1)	0.3161(3)	0.7420(3)	6.0(4)
C45	0.415(1)	0.2619(3)	0.6667(3)	4.9(3)
C46	0.336(1)	0.2889(4)	0.6488(4)	5.9(3)
C47	0.359(1)	0.3073(4)	0.6124(4)	7.8(4)
C48	0.472(2)	0.2993(4)	0.5958(4)	8.7(5)
C49	0.555(1)	0.2734(4)	0.6134(4)	7.6(4)
C50	0.524(1)	0.2540(4)	0.6483(4)	6.1(4)
C51	−0.027(1)	0.1967(3)	0.6815(3)	3.8(3)
C52	−0.0210(9)	0.2177(3)	0.6420(3)	3.5(2)
C54	0.1312(9)	0.1972(3)	0.5737(2)	2.6(2)
C55	0.098(1)	0.2293(3)	0.5488(3)	4.7(3)
C56	0.181(1)	0.2441(4)	0.5223(4)	6.3(4)
C57	0.301(1)	0.2288(4)	0.5242(4)	6.7(4)
C58	0.339(1)	0.1990(3)	0.5499(4)	5.6(3)
C59	0.249(1)	0.1829(3)	0.5755(3)	3.8(3)
C60	−0.1238(9)	0.1691(3)	0.5773(2)	2.7(2)
C61	−0.119(1)	0.1638(3)	0.5371(3)	3.8(3)
C62	−0.226(1)	0.1576(4)	0.5162(3)	4.7(3)
C63	−0.338(1)	0.1553(3)	0.5350(3)	4.7(3)
C64	−0.342(1)	0.1609(4)	0.5744(3)	4.9(3)
C65	−0.236(1)	0.1675(4)	0.5958(3)	4.2(3)
C78	0.191(1)	0.0759(5)	0.0519(6)	10.6(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)*[a^2*B(1,1)+b^2*B(2,2)+c^2*B(3,3)+ab(\cos \gamma)*B(1,2)+ac(\cos \beta)*B(1,3)+bc(\cos \alpha)*B(2,3)]$.

inter- and intramolecular separations below 3.6Å, and these near contacts tend to lock the perchlorate group, though high temperature factors for oxygens are found. The solvents of crystallization (CH_2Cl_2) is intercalated in the spaces between the perchlorates and the cations. The structure is held in three dimensional space by electrostatic and van der Waal's forces.

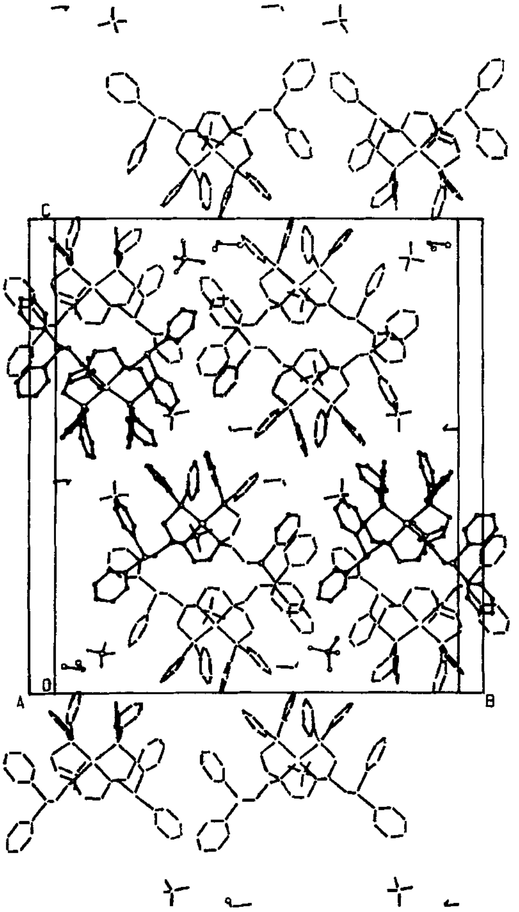

Figure 2 A view (projected down *c* axis) of complex (3)m [$Ni(BDPE)](ClO_4)_2$. CH_2Cl_2, showing crystal packing.

Table 5 Selected bond distances and angles for complex (3)

Bond distances (Å)		Bond angles (°)	
Ni(1)—P(2)	2.183(3)	P(2)—Ni(1)—N(17)	86.6(2)
Ni(1)—P(53)	2.191(3)	P(2)—Ni(1)—P(53)	100.0(2)
Ni(1)—N(53)	1.974(7)	N(17)—Ni(1)—N(35)	88.2(3)
Ni(1)—N(17)	1.989(7)	N(35)—Ni(1)—P(53)	83.8(3)
		P(2)—Ni(1)—N(35)	172.0(3)
		P(53)—Ni(1)—N(17)	170.7(2)

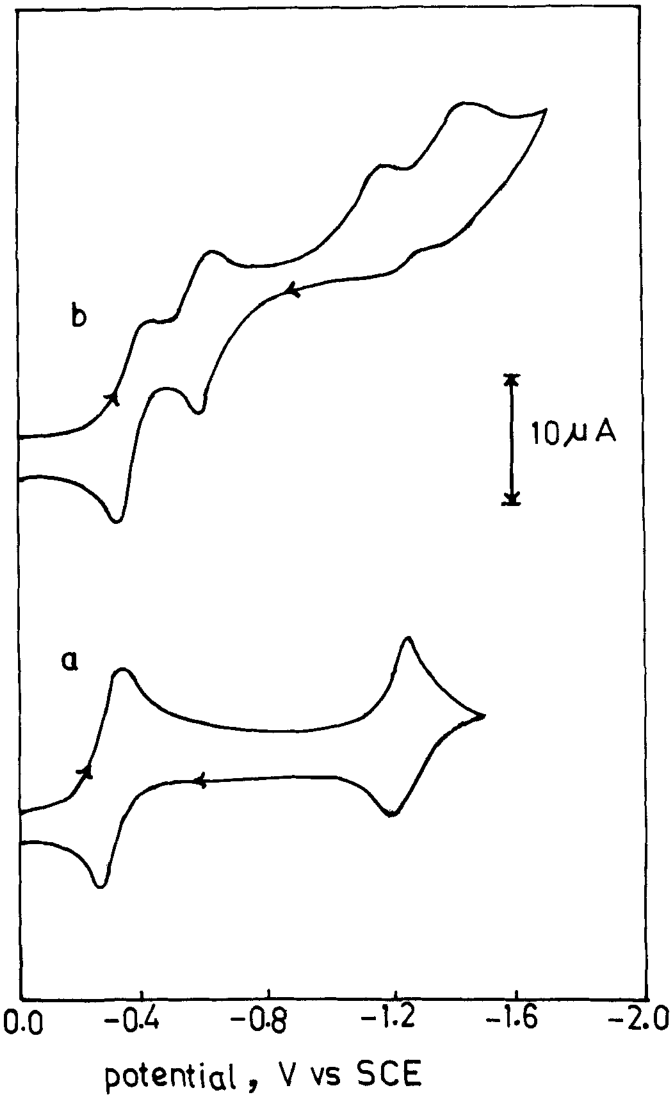

Figure 3 Cyclic voltammograms of (a) $[Ni(BDPE)](ClO_4)_2.CH_2Cl_2$, 4×10^{-3} M solution, and (b) $[Ni_2(BDPE)Cl_2](BPh_4)_2$, 3.5×10^{-3} M solution, in acetonitrile at 25°C.

Electrochemical Studies

Dc polarography, differential-pulse polarography (DPP) ad cyclic voltammetry of Ni(II) and Co(II) complexes were studied in the potential range 0 to − 1.8 V (*vs* SCE) in acetonitrile or dichloromethane. Figures 3 and 4 show cyclic voltammograms of $[Ni(BDPE)](ClO_4)_2.CH_2Cl_2$, $[Ni_2(BDPE)Cl_2](BPh_4)_2$ and $Co_2(BDPE)Cl_4$, respectively. Electrochemical data ($E_{1/2}$, ΔE_p and K_{com}) are listed in Table 6.

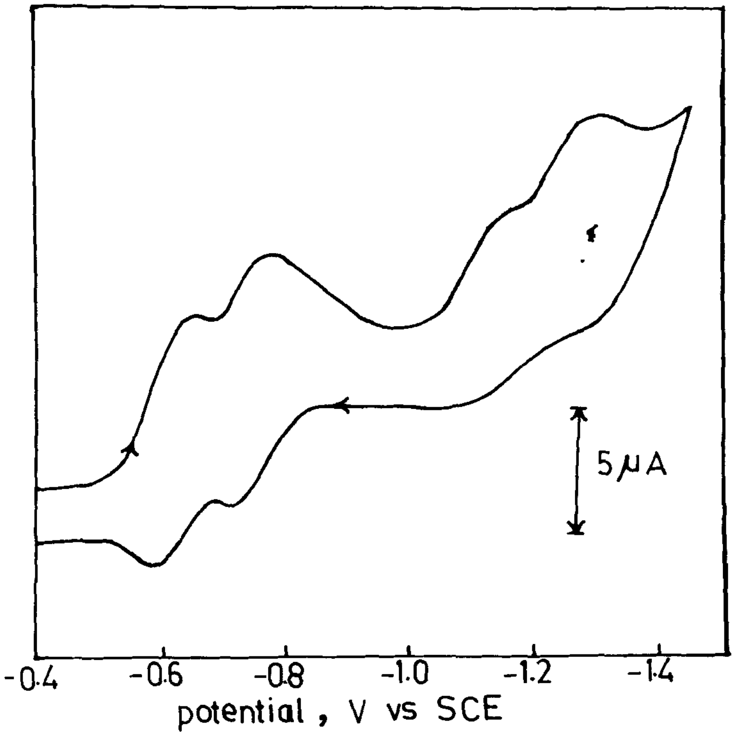

Figure 4 Cyclic voltammogram of $[Co_2(BDPE)Cl_4]$, 3×10^{-3} M solution, in dichloromethane at 25°C.

The electrochemical response observed for mononuclear Ni(II) ((3) and (5)) and Co(II) ((11) and (12)) complexes was similar. Two *quasi*-reversible one electron reductions in the ranges −0.28 to −0.43 V and −0.96 to −1.20 V were found. Reduction waves are confirmed by dc polarography studies. The *quasi*-reversible nature of the cyclic voltammetry is evident from the fact that the $E_{1/2}$ values were independent of scan rates, the ΔE_p values progressively increased when the scan rate was increased (100 to 500 mV s^{-1}) and the ratio of the peak currents due to cathodic and anodic sweeps were close to unity at different scan rates. The difference in potetials for the cathodic and anodic peaks is in the range 60–90 mV, as is consistent with a one electron redox process. The first wave (−0.28 to −0.43 V) for these mononuclear complexes may be assigned to Ni(II/I) or Co(II/I) redox couples and the second wave (−0.96 to −1.20 V) may be due to Ni(I/O) or Co(I/O). These results are quite similar to other reported values for Ni(II) with triphos[40] or dppe[41] ligands but slightly less negative as compared to Ni(II) and Co(II) complexes of PP_3, PP_2 and dppe ligands reported by DuBois *et al.*[7] However, the secondary coordinated ligand also shows some effect on redox potentials.

The dinuclear complexes of Ni(II) ((1) and (2)) and Co(II) ((6), (7), (9) and (10)) show two *quasi*-reversible redox couples in the potential range −0.38 to −0.72 V and two reduction waves (irreversible) in the range −0.93 to −1.37 V. These observations may be attributed to the sequential one electron transfer reactions as shown in scheme I.

Table 6 Comparison of cyclic voltametry data for Ni(II) and Co(II) complexes

Complex		Solvent	$E_{1/2}(II/I)/V^{a}$	$\Delta E_p(II/I)/mV^{b}$	$E_{1/2}(I/O)/V$	$\Delta E_p(I/O)/mV$	$K_{con}(II/I)^{e}$
$[Ni_2(BDPE)Cl_2](BPh_4)_2$	(1)	CH_3CN	−0.38, −0.60	60. 70	−1.12c(irr)^{d}	−1.44c(irr)^{f}	5.28×10^3
$[Ni_2(BDPX)Cl_2](BPh_4)_2$	(2)	CH_3CN	−0.40, −0.64	60, 80	−1.10c(irr), −1.40c(irr)^{f}		1.15×10^4
$[Ni(BDPE)](ClO_4)_2.CH_2Cl_2$	(3)	CH_3CN	−0.28	70	−1.18	80	
$[Ni(BDPX)](ClO_4)_2$	(5)	CH_3CN	−0.30	80	−1.20	80	
$[Co_2(BDPE)Cl_2](BPh_4)_2$	(6)	CH_2Cl_2	−0.45, 0.58	90, 100	−0.97c(irr), −1.12c(irr)^{f}		1.58×10^2
$[Co_2(BDPX)Cl_2](BPh_4)_2$	(7)	CH_2Cl_2	−0.46, −0.60	80, 100	−0.95c(irr), −1.10c(irr)^{f}		2.34×10^2
$[Co_2(BDPE)Cl_4]$	(9)	CH_2Cl_2	−0.60, −0.72	60, 80	−1.12c(irr), −1.28c(irr)^{f}		1.07×10^2
$[Co_2(BDPX)Cl_4]$	(10)	CH_2Cl_2	−0.59, −0.72	60, 70	−1.08c(irr), −1.24(irr)^{f}		1.58×10^2
$[Co(BDPE)](ClO_4)_2$	(11)	CH_3CN	−0.42	80	−0.96	100	
$[Co(BDPX)](ClO_4)_2$	(12)	CH_3CN	−0.43	80	−1.02	100	

$E_{1/2}=0.5(Epa+Epc)$ and potentials are referenced to the standard calomel electrode (SCE).

[b] $\Delta E_p=Epc-Epa$.

[d] The letter c indicates the cathodic peak for the irreversible wave.

[e] See text for calculation.

[f] The potentials listed for irreversible waves represent the potential of the peak current and not $E_{1/2}$.

Scheme I

$$\begin{tikzcd} \mathrm{M(II)-M(II)} \arrow[r, shift left, "+e"] & \mathrm{M(II)-M(I)} \arrow[l, shift left, "-e"] \arrow[r, shift left, "+e"] & \mathrm{M(I)-M(I)} \arrow[l, shift left, "-e"] \arrow[d, "+e"] \\ & \mathrm{M(O)-M(O)} & \mathrm{M(I)-M(O)} \arrow[l, "+e"'] \end{tikzcd}$$

Similar sequential one electron transfer for M(II/I) redox couples have also been observed for a number of binuclear Cu(II)[42-44] and Ni)II)[44,45] complexes. Dinuclear Ru(III) complexes too exhibit sequential one electron transfer processes for Ru(III/II) redox couples.[46] Such couples are ofte used to determine the relative stabilities of mixed valence species.[42-46] Thus, the stability of the mixed valence species ca be expressed in terms of the conproprotionation constant k_{con} of the following equiplibrium,

$$\mathrm{M(II)-M(II)+M(I)-M(I)} \overset{K_{con}}{\rightleftharpoons} \mathrm{2M(II)-M(I)}$$

$$K_{com}=\frac{[\mathrm{M(II)-M(I)}]^2}{[\mathrm{M(II)-M(II)}][\mathrm{M(I)-M(I)}]}$$

$$k_{con}=\exp(nF\Delta E/RT)$$

where $\Delta E=E^1_{1/2}-E^2_{1/2}$. The K_{con} values for M(II/I) (M = Ni, Co) for the dinuclear complexes are listed in Table 6. The values are lower than reported values for Cu(II) ($\sim 3\times 10^6$ to $\sim 4\times 10^{11}$)[42,43] and Ni(II) (1×10^{11})[45] [for M(II/I)].

The $E_{1/2}$ values for Co(II/I) of (9) and (10) are more negative compared to other dinuclear complexes. This difference may be due to molecular charge; complexes (1), (3), (6) and (7) being dicationic accept an electron more easily due to electrostatic effects compared to neutral complexes (9) and (10). The M(I/O) couples for mononuclear complexes are *quasi*-reversible whereas dinuclear complexes show two irreversible reduction waves (Figs 4 and 5). This difference may be due to the fact that the dinuclear complexes, which contain bonded chloride, undergo M—Cl bond rupture as soon as M(I) reduces to M(O), whereas in mononuclear complexes no anionic species is bonded to the metal and due to the strong chelating effect of the NNPP set, the cationic species remain intact even when M(I) is reeuced to M(O).

SUPPLEMENTARY DATA

Full lists of bond lengths and angles, torsion angles, hydrogen positions, thermal parameters and observed and calculated structure factors are available from K.V.

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