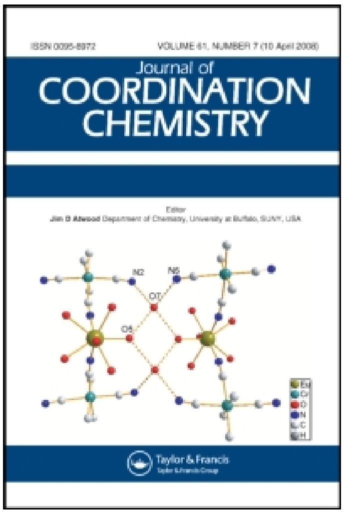

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REACTIONS OF TRANSITION METAL THIOLATO UNITS IV.* FORMATION OF PHOSPHINE-CONTAINING COBALT OR NICKEL COMPLEXES WITH *iso*-MALEONITRILE-DITHIOLATE

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The reaction of M^{2+} (M = Co or Ni) with K_2(*i*-mnt) and phosphine forms chelated ternary coordination compounds (**1**)–(**4**). The crystal structures of Ni(*i*-mnt)(dppmSe) (**1**) (in the presence of Se) and $(^nBu_4N)[Co(i\text{-mnt})_2(PBu^n_3)_2]$ (**2**) were determined by single-crystal X-ray diffraction analyses; (**1**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.002(3)$, $b = 19.568(11)$, $c = 12.456(5)$ Å, $\beta = 92.22(3)°$, $V = 2923.4$ Å^3, $Z = 2$, R (R_w) = 0.051 (0.062). The distorted, square planar Ni atom forms two individual chelate rings with the two bidentate ligands. Complex (**2**) crystallizes in space group $P\bar{1}$ with $a = 10.682(2)$, $b = 28.496(6)$, $c = 9.959(2)$ Å, $\alpha = 91.31(2)$, $\beta = 97.71(2)$, $\gamma = 83.68(2)°$, $V = 2986(1)$ Å^3, $Z = 2$, R (R_w) = 0.060 (0.072). The octahedral Co(III) ion in (**2**) has an elongated structure with two monodentate phosphines in axial positions and *i*-mnt groups chelating in the equatorial plane. Spectroscopic characterization was performed where appropriate.

Keywords: Phosphine-thiolato cobalt complex; phosphine-thiolato nickel complex; crystal structure; *iso*-maleonitrile dithiolate; *bis*(diphenylphosphino)methane monoselenide

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[*] Part III of this series: B.S. Kang, H.R. Gao, Z.N. Chen, Y.X. Tong, H.Q. Liu, B.M. Wu and T.C.W. Mak, *Polyhedron*, **16**, 1731 (1997).

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INTRODUCTION

Transition metal thiolato complexes containing a phosphine as co-ligand have been studied and reviewed recently.[1] Particular interest has been focused on complexes containing 1,2-bidentate thiolates with tertiary phosphines which could form stable clusters with three,[2] four,[3] or eight[4] nuclei. However, ternary complexes with 1,1′-dithiolato ligands such as *i*-mnt (*iso*-maleonitrile dithiolate) or Hmbt (2-mercaptobenzothiazole)[5] are not much studied for cobalt or nickel, although silver[6] and copper[7] have been shown to form multinuclear cluster complexes. We hereby report some of these complexes and the crystal structures of Ni(*i*-mnt)(dppmSe) (**1**) and (^{n}Bu$_4$N)[Co(*i*-mnt)$_2$(PBu$^n_3$)$_2$] (**2**).

EXPERIMENTAL

Anhydrous cobalt chloride, nickel chloride hexahydrate, diphenylphosphinomethane (dppm), triphenylphosphine (PPh$_3$), and tri-*n*-butylphosphine (PBu$^n_3$) were commercially available and used as received. Dipotassium *iso*-maleonitrile dithiolate (K$_2$(*i*-mnt) · H$_2$O) was synthesized according to a literature method.[8] IR spectra were recorded on a Nicolet Magna 750 FTIR spectrophotometer in KBr pellets and NMR spectra were obtained using a Varian Unity 500 spectrometer operating at 499.98 MHz for ^{1}H, 125.71 MHz for ^{13}C and 202.36 MHz for ^{31}P. Chemical shift data are in ppm, referred to internal Me$_4$Si for ^{1}H and ^{13}C and to external 85% H$_3$PO$_4$ for ^{31}P.

Ni(*i*-mnt)(dppmSe) (1)

To a K$_2$(*i*-mnt) · H$_2$O (0.11 g, 0.5 mmol) solution in 15 cm^3 of EtOH and 5 cm^3 of MeCN was added NiCl$_2$ · 6H$_2$O (0.12 g, 0.5 mmol) with stirring. Dppm (0.19 g, 0.5 mmol) and Se powder (0.04 g, 0.5 mmol) were added over a few minutes and the solution soon turned dark brown and gave a large amount of precipitates. DMF (10 cm^3) was added to dissolve the precipitate. The solution was stirred for 4 h and filtered. The dark-red filtrate left at 5°C overnight gave reddish brown crystals. Yield 40%. IR (KBr, cm^{-1}): 476m, 488m, 511m, 534s, 685m, 739s, 791m, 897m, 935w, 999w, 1097s, 1151w, 1387w, 1417vs, 1437s, 2208s, 2897w, 2949m, 3056vw.

(Bu$_4$N)[Co(*i*-mnt)$_2$(PBu$^n_3$)$_2$] (2)

Equimolar amounts of anhydrous CoCl$_2$ (0.13 g, 1.0 mmol) and K$_2$(*i*-mnt) · H$_2$O (0.22 g, 1.0 mmol) in 15 cm^3 of EtOH were added to PBu$^n_3$ (0.25 cm^3, 1.0 mmol) with stirring at room temperature. After reaction for 2 h, ${}^{n}Bu_4NBF_4$ was added and the solution was filtered. The filtrate gave dark brown crystals of (**2**) after standing at 5°C for several days. Yield 36%.

$Ni(i\text{-mnt})(PPh_3)_2$ (3)

To a solution of $K_2(i\text{-mnt}) \cdot H_2O$ (0.11 g, 0.5 mmol) in 10 cm^3 of EtOH and 5 cm^3 of MeCN was added 0.12 g of $NiCl_2 \cdot 6H_2O$ (0.5 mmol) with stirring. The solution turned dark brown and gave reddish brown precipitates within a few minutes when PPh_3 (0.26 g, 1.0 mmol) was added. DMF (20 cm^3) was added to dissolve the precipitates and the solution was filtered. The dark red filtrate was kept at 5°C to give dark red crystals of the product. Yield 62%. *Analysis*, Calcd. for $C_{40}H_{30}N_2NiP_2S_2$ (%): Ni, 8.12; P, 8.56; S, 8.86. Found: Ni, 7.78; P, 8.55; S, 9.16. IR (KBr, cm^{-1}): 494m, 511s, 521w, 530s, 688s, 700s, 889m, 971m, 1095s, 1184m, 1321w, 1380w, 1431s, 1479m, 1662w, 2208s, 3051w, 3074w. Preliminary single-crystal X-ray diffraction studies gave unit cell parameters $a = 18.1704$, $b = 10.8431$, $c = 9.1579$ Å, $\beta = 78.417°$, $V = 1767$ Å^3, similar to those reported for $Ni(i\text{-mnt})(PPh_3)_2$.[9]

$Ni(i\text{-mnt})(PBu^n_3)_2$ (4)

To a mixture of 20 cm^3 of EtOH and 10 cm^3 of MeCN was added $NiCl_2 \cdot 6H_2O$ (0.12 g, 0.5 mmol) and $K_2(i\text{-mnt}) \cdot H_2O$ (0.11 g, 0.5 mmol). The solution turned dark brown in a short time and PBu^n_3 (0.25 cm^3, 1.0 mmol, $d = 0.812$ g cm^{-3}) was added with continuous stirring for 10 h, during which the solution turned dark red. The filtrate gave orange blocky crystals of the product when evaporated in air. Yield 60%. Analysis, Calcd for $C_{28}H_{54}N_2NiP_2S_2$ (%): C, 55.70; H, 8.60; N, 4.64; Ni, 9.74. Found: C, 55.23; H, 8.87; N, 4.46; Ni, 9.42. IR (KBr, cm^{-1}): 455w, 476w, 613w, 719s, 797s, 895s, 1022s, 1047s, 1094vs, 1261s, 1379m, 1440s, 2210s, 2872m, 2932m, 2959m. Preliminary single-crystal X-ray diffraction analysis gave unit cell parameters $a = 16.9713$, $b = 20.4895$, $c = 22.1352$ Å, $\beta = 110.2513°$, $V = 7221$ Å^3. Due to fast deterioration of the crystal, not enough reflections were collected for a crystal structure solution.

Intensity Data Collection and Structure Analysis

Single crystals of suitable size were selected and coated with epoxy resin and mounted on glass fibres in a random orientation. Diffraction data were collected at room temperature (23°C) on an Rigaku MSC/AFC5R diffractometer equipped with a graphite monochromator with Mo Kα radiation ($\lambda = 0.71069$ Å). For complexes (**1**) and (**2**), after data reduction

TABLE I Summary of crystal data and data collection parameters

Compound	**1**	**2**
Formula	$C_{29}H_{22}N_2NiP_2SeS_2$	$C_{46}H_{90}N_7CoP_2S_4$
F.W.	661.6	990.4
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a, Å	12.002(3)	10.682(2)
b, Å	19.568(11)	28.496(6)
c, Å	12.456(5)	9.959(2)
α, °		91.31(2)
β, °	92.22(3)	97.71(2)
γ, °		83.68(2)
V, Å^3	2923.4	2986(1)
Z	2	2
Dc, g·cm^{-3}	0.75	1.10
μ, cm^{-1}	14.0	5.06
F(000)	736	1072
Crystal dimensions, mm^3	0.10 × 0.12 × 0.40	0.50 × 0.50 × 0.35
Scan mode	ω	ω
Scan range 2θ, °	50.0	50.0
R_{int}	0.035	0.0172
No. of reflections refined with $I > 3.0\ \sigma\ (I)$	2521	3655
No. of variables	334	544
Highest peak in final diff. map, e Å^{-3}	0.31	0.34
R	0.051	0.060
R_w	0.062	0.072

(including correction for fluctuation of monitored reflections, LP factors and empirical absorption), the remaining unique reflections with $I > 3\sigma\ (I)$ were used for subsequent structure solution and refinement. Crystal data and data collection parameters are summarized in Table I. The structures were solved by direct methods and Fourier syntheses and the coordinates of all the non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were included as fixed contributions isotropically to the structure factor calculations but not refined. Calculations were performed on a COMPAQ PL4/50 computer with MolEN/PC software.[10]

RESULTS AND DISCUSSION

Synthesis

In our continuing study of the construction of multinuclear cluster complexes from simple transition metal thiolato structural units, it has been observed that some thiolato-phosphine moieties such as $M(bdt)_2(PR_3)$

(M = Fe, Co; bdt = 1,2-benzenedithiolate) or $M(mp)_2(PR_3)$ (M = Co, Ni; mp = 2-mercaptophenolate) of general formula ML_2L' with L = 1,2-bidentate thiolato ligand and L′ = monodentate phosphine, are good construction units or building blocks.[2–4] However, when L'_2 is a bidentate phosphine such as in Co(bdt)(dppe)[11] (dppe = 1,2-*bis*(diphenylphosphino)-ethane) or Ni(tdt)(dppm)[11] (tdt = 3,4-toluenedithiolate, dppm = 1,2-*bis*-(diphenylphosphino)methane), the species MLL'_2 formed is not reactive due to the extreme stability of the mononuclear complexes, although dinuclear complexes have been reported for gold(I).[12] Thus, it is a preliminary consideration that structural units of cobalt or nickel with both bidentate thiolate and phosphine ligands forming 4-, 5-, or 6-membered chelate rings, would be unable to undergo a construction reaction due to the limitation of the size of the central metals. Similarly, when the 1,1′-bidentate *i*-mnt was employed, mononuclear ternary complexes (**1**)–(**4**) of formula $NiLL'_2$ or $[CoL_2L'_2]^{1-}$, where L = *i*-mnt, and L'_2 = dppmSe, $(PBu^n_3)_2$, or $(PPh_3)_2$,[9] were obtained depending on reaction conditions. Whether these structural units will undergo further reaction is not yet known.

M	L	L'_2	Complex
Ni	*i*-mnt	dppmSe	**1**
Ni	*i*-mnt	$(PPh_3)_2$	**3**
Ni	*i*-mnt	$(PBu^n_3)_2$	**4**
Co	*i*-mnt	$(PBu^n_3)_2$	**2**

In the synthesis of complex (**1**), selenium powder was added originally for the purpose of oxidation of dppm to give dppmSe, which renders the two P atoms different and would give a rich coordination behaviour for the phosphine ligand. The reaction of Se with dppm has long been documented in the literature[13,14] and pure dppmSe is formed with a 1 : 1 molar ratio of Se and dppm without contamination by $dppmSe_2$; a mixture of dppmS and $dppmS_2$ is always formed when sulfur is used despite use of different mol ratios. In this way, unsymmetrically Se-substituted dppm can be obtained. More work is underway to understand the generality of the coordination behaviour of the P=Se bond in dppmSe.

Structures

Atomic coordinates of the non-hydrogen atoms of complexes (**1**) and (**2**) are listed in Tables II and III, respectively. The molecular structures of (**1**) and (**2**) are shown in Figures 1 and 2, respectively, with selected atomic distances and bond angles listed in Tables IV and V, respectively. The central

TABLE II Positional and thermal parameters for Ni(*i*-mnt)(dppmSe) (**1**)

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
Se	0.01256(8)	0.17687(5)	0.12972(9)	4.34(2)
Ni	0.06877(9)	0.07034(6)	0.18819(9)	3.27(2)
S(1)	−0.0936(2)	0.0267(1)	0.1295(2)	4.54(6)
S(2)	0.0940(2)	−0.0374(1)	0.2225(2)	4.16(5)
P(1)	0.2280(2)	0.1026(1)	0.2587(2)	3.04(5)
P(2)	0.1544(2)	0.2394(1)	0.1787(2)	3.38(5)
N(1)	−0.2788(6)	−0.1240(4)	0.0558(6)	5.2(2)
N(2)	0.0178(7)	−0.2230(4)	0.2030(7)	6.0(2)
C(1)	0.2715(6)	0.1821(4)	0.1961(7)	3.1(2)
C(2)	−0.0347(7)	−0.0506(5)	0.1623(7)	3.5(2)
C(3)	−0.0826(6)	−0.1129(4)	0.1433(6)	3.1(2)
C(4)	−0.1914(7)	−0.1198(5)	0.0931(7)	3.9(2)
C(5)	−0.0268(8)	−0.1738(5)	0.1763(7)	4.2(2)
C(11)	0.2218(6)	0.1202(5)	0.4008(7)	3.5(2)
C(12)	0.2927(7)	0.1658(5)	0.4534(7)	4.4(2)
C(13)	0.2915(8)	0.1756(6)	0.5620(8)	5.9(3)
C(14)	0.2164(9)	0.1416(7)	0.6206(8)	7.1(3)
C(15)	0.1444(8)	0.0964(7)	0.5711(8)	6.6(3)
C(16)	0.1468(8)	0.0866(6)	0.4608(8)	5.2(3)
C(21)	0.3500(6)	0.0481(4)	0.2513(7)	3.1(2)
C(22)	0.4090(9)	0.0423(6)	0.1611(8)	6.1(3)
C(23)	0.501(1)	−0.0009(7)	0.1562(9)	7.7(3)
C(24)	0.5327(8)	−0.0374(6)	0.2441(9)	5.8(3)
C(25)	0.474(1)	−0.0333(6)	0.3346(9)	6.8(3)
C(26)	0.3831(8)	0.0090(5)	0.3387(9)	5.7(3)
C(31)	0.1888(7)	0.3004(4)	0.0760(7)	3.8(2)
C(32)	0.2941(8)	0.3258(6)	0.0723(9)	5.6(3)
C(33)	0.322(1)	0.3711(6)	−0.008(1)	7.1(3)
C(34)	0.243(1)	0.3896(6)	−0.0849(9)	6.9(3)
C(35)	0.138(1)	0.3631(6)	−0.0823(9)	7.3(3)
C(36)	0.11(8)	0.3184(5)	−0.0019(8)	5.5(3)
C(41)	0.1341(7)	0.2825(5)	0.3051(7)	4.1(2)
C(42)	0.0511(8)	0.2637(6)	0.3713(8)	5.6(3)
C(43)	0.0421(9)	0.2926(7)	0.471(1)	7.8(3)
C(44)	0.118(1)	0.3403(6)	0.5031(9)	8.2(3)
C(45)	0.202(1)	0.3617(6)	0.4368(9)	7.1(3)
C(46)	0.2085(8)	0.3322(5)	0.3372(8)	5.2(2)

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

Ni(II) atom of complex (**1**) is located in a distorted square planar environment, just like all the other NiLL′$_2$ type complexes[9,15,16] listed in Table VI, in which the atoms Ni, S(1), S(2), Se and P(1) are nearly co-planar. The two bidentate ligands dppmSe and *i*-mnt form 5- and 4-membered chelate rings with the Ni atom, respectively. The ring NiS(2)S(1)C(2) is nearly planar with the bond Ni–S(1) *trans* to P(1) being slightly longer than Ni–S(2), which is *trans* to the bond Ni–Se, showing the *trans* influence of phosphine.

TABLE III Positional and thermal parameters for (^{n}Bu$_4$N)[Co(i-mnt)$_2$(PBu$^n_3$)$_2$] (2)

Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
Co(1)	0.000	0.500	0.000	5.06(5)
S(1)	0.1658(3)	0.44501(9)	0.0627(3)	5.74(8)
S(2)	−0.0687(3)	0.45833(9)	0.1633(3)	5.79(8)
P(1)	−0.0777(3)	0.4503(1)	−0.1712(3)	5.92(8)
N(1)	0.329(1)	0.3375(5)	0.249(2)	14.1(6)
N(2)	−0.046(1)	0.3494(4)	0.387(1)	9.7(4)
C(1)	0.071(1)	0.4234(3)	0.167(1)	5.2(3)
C(2)	0.109(1)	0.3834(4)	0.245(1)	9.3(4)
C(3)	0.236(2)	0.3574(5)	0.247(1)	9.0(5)
C(4)	0.021(1)	0.3649(4)	0.327(1)	7.2(4)
C(5)	−0.190(1)	0.4124(4)	−0.120(1)	7.9(4)
C(6)	−0.315(1)	0.4377(4)	−0.088(1)	7.9(4)
C(7)	−0.399(2)	0.4040(6)	−0.034(2)	14.6(7)
C(8)	−0.518(1)	0.4252(6)	−0.004(2)	15.2(7)
C(9)	0.038(1)	0.4049(4)	−0.232(1)	7.5(4)
C(10)	0.145(1)	0.4213(4)	−0.297(1)	7.7(4)
C(11)	0.241(1)	0.3807(5)	−0.329(1)	10.4(5)
C(12)	0.348(2)	0.3959(6)	−0.400(2)	15.4(7)
C(13)	−0.162(1)	0.4775(4)	−0.326(1)	6.7(3)
C(14)	−0.224(1)	0.4446(5)	−0.433(1)	10.0(5)
C(15)	−0.309(2)	0.4677(6)	−0.540(2)	13.1(6)
C(16)	−0.379(2)	0.4362(7)	−0.635(2)	16.6(8)
Co(2)	0.000	0.000	0.000	3.93(5)
S(3)	−0.0706(2)	0.05773(8)	−0.1552(2)	4.60(7)
S(4)	−0.1690(2)	0.04017(8)	0.0846(2)	4.60(6)
P(2)	0.1414(3)	0.04750(8)	0.1174(2)	4.34(7)
N(3)	−0.306(1)	0.1618(3)	−0.301(1)	9.1(4)
N(4)	−0.4567(8)	0.1272(3)	0.0740(9)	6.7(3)
C(17)	−0.1842(9)	0.0747(3)	−0.0548(9)	4.2(2)
C(18)	−0.2846(9)	0.1109(3)	−0.086(1)	7.3(3)
C(19)	−0.297(1)	0.1397(4)	−0.207(1)	6.2(3)
C(20)	−0.383(1)	0.1202(3)	0.002(1)	4.9(3)
C(21)	0.1807(9)	0.0979(3)	0.0226(8)	4.5(3)
C(22)	0.2537(9)	0.0823(3)	−0.097(1)	5.7(3)
C(23)	0.279(1)	0.1238(4)	−0.177(1)	6.6(3)
C(24)	0.365(1)	0.1093(4)	−0.286(1)	9.4(4)
C(25)	0.2980(9)	0.0202(3)	0.1919(9)	5.3(3)
C(26)	0.386(1)	0.0510(4)	0.274(1)	6.2(3)
C(27)	0.518(1)	0.0252(4)	0.312(1)	7.8(4)
C(28)	0.611(1)	0.0548(5)	0.400(1)	10.4(5)
C(29)	0.083(1)	0.0804(3)	0.2610(9)	5.9(3)
C(30)	0.056(1)	0.0508(4)	0.377(1)	6.7(3)
C(31)	0.012(2)	0.0786(6)	0.494(2)	16.6(9)
C(32)	−0.048(2)	0.1180(6)	0.501(2)	17.0(8)
N(5)	−0.3337(8)	0.2464(3)	0.2801(8)	5.8(3)
C(33)	−0.219(1)	0.2181(3)	0.231(1)	6.6(3)
C(34)	−0.127(1)	0.2469(4)	0.174(1)	7.8(4)
C(35)	−0.018(1)	0.2139(5)	0.127(1)	10.2(5)
C(36)	0.082(2)	0.2402(6)	0.075(2)	13.3(6)
C(37)	−0.297(1)	0.2810(3)	0.393(1)	6.7(4)
C(38)	−0.214(1)	0.2573(4)	0.515(1)	8.8(4)
C(39)	−0.207(2)	0.2941(5)	0.629(1)	12.6(6)
C(40)	−0.132(2)	0.2749(6)	0.748(2)	21.74(8)
C(41)	−0.410(1)	0.2767(3)	0.165(1)	6.0(3)

TABLE III (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
C(42)	−0.462(1)	0.2494(4)	0.042(1)	8.9(4)
C(43)	−0.534(1)	0.2813(4)	−0.065(1)	11.2(5)
C(44)	−0.588(2)	0.2554(5)	−0.187(2)	16.5(8)
C(45)	−0.414(1)	0.2103(3)	0.328(1)	6.6(4)
C(46)	−0.534(1)	0.2314(4)	0.382(1)	8.2(4)
C(47)	−0.619(1)	0.1930(5)	0.399(1)	10.4(5)
C(48)	−0.741(2)	0.2127(6)	0.457(1)	12.4(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [*a*2 * *B*(1, 1) + 2^{b} * *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)].

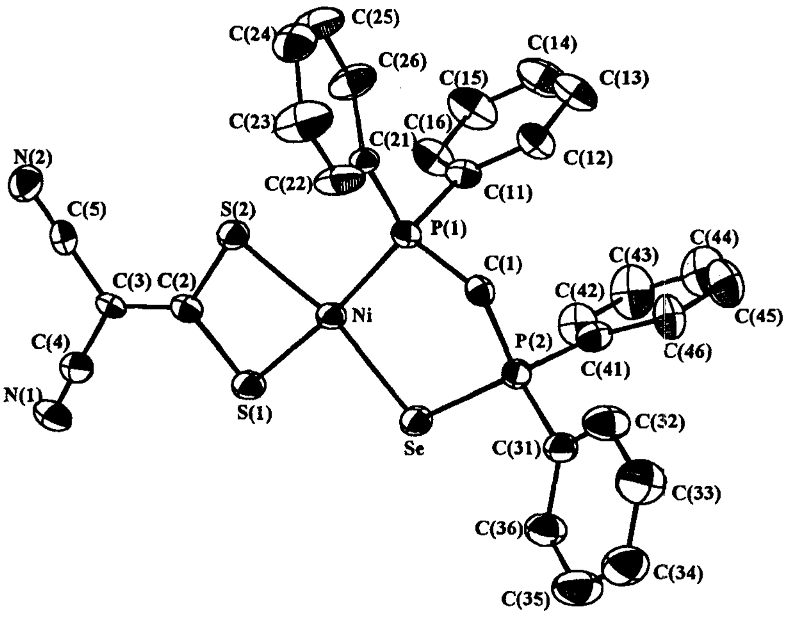


FIGURE 1 Molecular structure of Ni(*i*-mnt)(dppmSe) (**1**).

The ring $\overline{\mathrm{NiP(1)C(1)P(2)Se}}$ is not planar but puckered relative to Ni–Se with C(1) being 0.25 Å above and P(1) and P(2) (average 0.16 Å) below it. The bond Ni–Se (2.301 Å) is quite close to that reported for $[Ni_3Se_2(dppe)_3]^{2+}$ (2.311 Å),[17] although the inorganic Se atoms in the latter

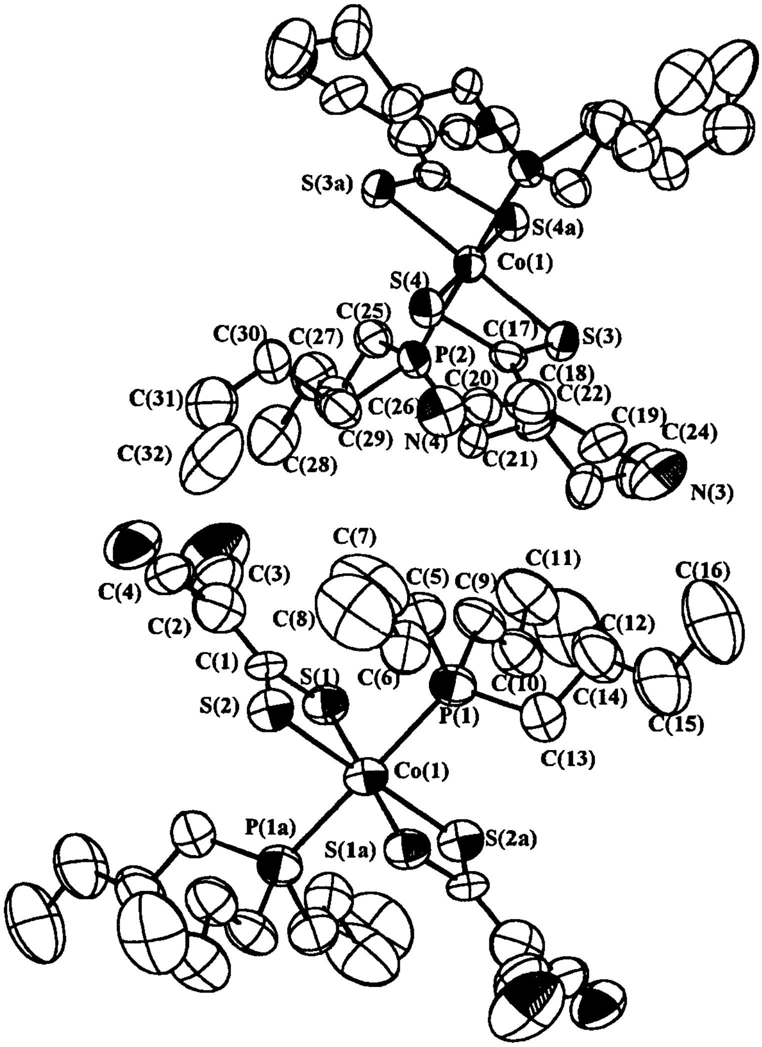
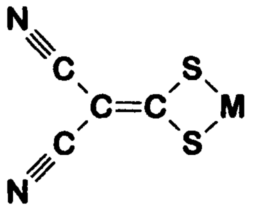


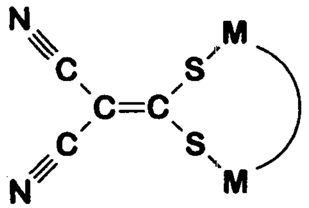
FIGURE 2 Molecular structure of (^{n}Bu$_4$N)[Co(i-mnt)$_2$(PBu$^n_3$)$_2$] (2).

complex in bridging positions should behave differently to that in complex (1). Table VI shows changes of structural parameters with the size of the chelate rings.

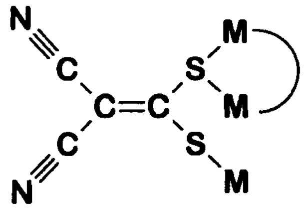
The ligand *i*-mnt could ligate to metal atoms in coordination modes I–IV, as follows, showing terminal I[18] or bridging ligation II–IV[12,19,20] in versatile fashion. Both complex (1) and (2) showed *i*-mnt in coordination mode I.



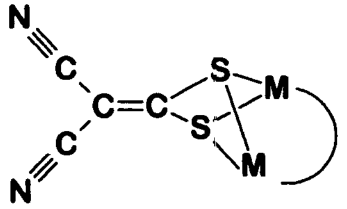
I



II



III

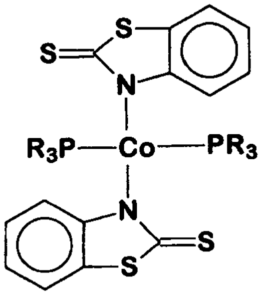


IV

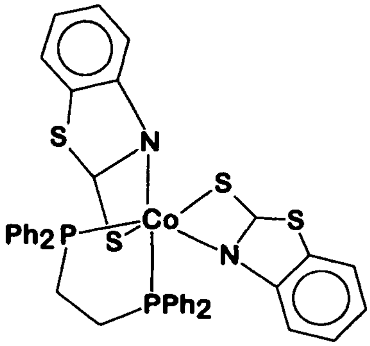
Complex (**2**) is an octahedrally coordinated cobalt(III) complex with the two *i*-mnt ligands in the anion in equatorial positions and the two axial sites occupied by two monodentate phosphine ligands. This is an addition to the set of mononuclear Co complexes[5,11,21] with mixed phosphine and thiolato ligands, but of different structural geometries (see Table VII). Among the ternary cobalt complexes $(Bu_4N)[Co(i\text{-mnt})_2(PBu^n_3)_2]$ (**2**), Co(*N*-mbt)$_2$ $(PBu^n_3)_2$[5] (**5**), Co(*N*,*S*-mbt)$_2$(dppe)[5] (**6**), Co(bdt)(dppe)[11] (**7**), and $(PHBu^n_3)[Co(bdt)_2(PBu^n_3)]$[21] (**8**), (**2**) and (**6**) have the cobalt atom in octahedral geometry, (**5**) and (**7**) in square planar environment, and (**8**) in square pyramidal. According to the data presented in Table VII, the following structural features are found:

(1) Octahedral, square pyramidal, and square planar geometries are all possible for cobalt with mixed phosphine and thiolato ligands. Whether the phosphine ligand is mono- or bidentate does not affect the coordination geometry.

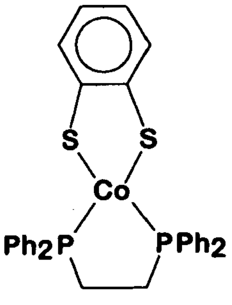
(2) The geometry of the central metal atom is controlled mainly by the bidentate thiolates. Table VII shows that 4-membered chelate rings formed by *i*-mnt and *N*,*S*-mbt as in complexes (**2**) and (**6**) afford less steric congestion and would allow octahedral coordination.



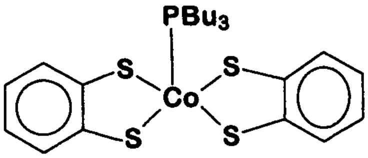
(5)



(6)



(7)



(8)

(3) The data in Table VII show that no regularities are followed for these types of complexes; structural data vary severely among 4- and 5-membered chelate rings and change drastically for different types of thiolato and phosphine ligands.

More extensive work should be done before any conclusion could be drawn concerning the building block character of these complexes or the possibility of further construction into multinuclear cluster complexes, although species similar to (**8**) have been shown to be useful building blocks for a series of tri-,[2] tetra-,[3] and octanuclear[4] cluster complexes. Complex (**4**) has been shown by elementary analyses to be of composition NiLL$'_2$. Without complete structural data, its molecular structure has been deduced by spectroscopic methods (see below).

TABLE IV Selected atomic distances (Å) and bond angles (°) for Ni(*i*-mnt)(dppmSe) (**1**)

Atoms	*Distance*	*Atoms*	*Distance*
Se–Ni	2.301(1)	Se–P(2)	2.165(2)
Ni–S(1)	2.225(3)	Ni–S(2)	2.170(3)
Ni–P(1)	2.167(2)	S(1)–C(2)	1.71(1)
S(2)–C(2)	1.711(8)	P(1)–C(1)	1.825(9)
P(2)–C(1)	1.805(9)	N(1)–C(4)	1.13(1)
N(2)–C(5)	1.14(1)	C(2)–C(3)	1.36(1)
C(3)–C(4)	1.43(1)	C(3)–C(5)	1.42(1)
Atoms	*Angle*	*Atoms*	*Angle*
Ni(1)–Se–P(2)	101.84(8)	Se–Ni–S(1)	90.06(8)
Se–Ni–S(2)	168.43(8)	Se–Ni–P(1)	96.18(8)
S(1)–Ni–S(2)	78.82(9)	S(1)–Ni–P(1)	173.1(2)
S(2)–Ni–P(1)	95.09(9)	Ni–S(1)–C(2)	85.0(3)
Ni–S(2)–C(2)	86.8(3)	Ni–P(1)–C(1)	109.7(3)
Se–P(2)–C(1)	106.5(3)	S(1)–C(2)–S(2)	109.1(5)

TABLE V Selected atomic distances (Å) and bond angles (°) for (^{n}Bu$_4$N)[Co(*i*-mnt)$_2$-(PBu$^n_3$)$_2$] (**2**)

Atoms	*Distance*	*Atoms*	*Distance*
Co(1)–S(1)	2.263(2)	Co(2)–S(3)	2.279(2)
Co(1)–S(2)	2.279(3)	Co(2)–S(4)	2.278(2)
Co(1)–P(1)	2.317(3)	Co(2)–P(2)	2.320(2)
S(1)–C(1)	1.71(1)	S(3)–C(17)	1.70(1)
S(2)–C(1)	1.70(1)	S(4)–C(17)	1.700(9)
P(1)–C(5)	1.83(1)	P(2)–C(21)	1.853(9)
P(1)–C(9)	1.84(1)	P(2)–C(25)	1.833(9)
P(1)–C(13)	1.82(2)	P(2)–C(29)	1.83(1)
N(1)–C(3)	1.09(2)	N(3)–C(19)	1.12(2)
N(2)–C(4)	1.12(2)	N(4)–C(20)	1.13(1)
Atoms	*Angle*	*Atoms*	*Angle*
S(1)–Co(1)–S(2)	76.3(1)	S(3)–Co(2)–S(4)	76.18(9)
S(1)–Co(1)–P(1)	90.15(9)	S(3)–Co(2)–P(2)	91.33(8)
S(2)–Co(1)–P(1)	92.6(2)	S(4)–Co(2)–P(2)	92.31(9)
Co(1)–S(1)–C(1)	86.4(3)	Co(2)–S(3)–C(17)	86.1(3)
Co(1)–S(2)–C(1)	86.1(4)	Co(2)–S(4)–C(17)	86.1(3)
S(1)–C(1)–S(2)	110.9(6)	S(3)–C(17)–S(4)	111.6(5)

Spectroscopic Studies

^{1}H NMR data for (**1**) listed in Table VIII show that the CH$_2^-$ of dppmSe appears as a triplet caused by overlapping of a doublet of doublets centred at 5.10 ppm, due to the influences of the two different phosphorus atoms ($^2J_{\mathrm{Pep-H}}$ and $^2J_{\mathrm{PSe-H}}$). The phenyl protons are gathered near 7.0 ppm as usually observed for diamagnetic molecules. The two phosphorus atoms P$_{\mathrm{ep}}$ (ep for electron pair) and P$_{\mathrm{Se}}$ appear at 44.58(d) and 43.28(d) ppm,

TABLE VI Comparison of structural data of some NiLL′ type complexes (L = bidentate thiolate, L′ = phosphine)

Complex[a]	(Å)			*Chelate ring* (°)			*Ref.*
	Ni–S	*Ni–P*	*C–S*	*S–Ni–X*	*Ni–P–C*	*Ni–S–C*	
Ni(*i*-mnt)(dppmSe)	2.198	2.167	1.711	78.82	109.7	85.9	this work
Ni($S_2N(CH_2)_2O$)(dppe)	2.204	2.164	1.710	79.36	108.54	84.86	15
Ni(tdt)(dppm)	2.145	2.181	1.752	91.9	95.5	103.7	9
Ni(edt)(dppe)	2.176	2.153	1.864	92.80	109.3	101.5	16
Ni(tsal)(dppe)	2.167	2.193	1.753	96.10	108.9	109.6	9

[a] tdt = 3,4-toluenedithiolate, edt = 1,2-ethanedithiolate, tsal = thiosalicylate, dppm = 1,2-*bis*(diphenylphosphino)methane, dppe = 1,2-*bis*(diphenylphosphino)ethane.

respectively. Due to the low abundance of ^{77}Se (7.58%), signals caused by P–Se coupling appear weakly at 45.9 and 40.7 ppm, again as two doublets. The coupling constants $^1J_{P-Se} = 526$ Hz and $^2J_{P-P} = 69$ Hz are comparable to those reported.[14] The ^{13}C NMR of *i*-mnt in complex (**1**) showed resonances at 205.65 ($C(S)_2$), 113.85 and 115.52 (two C≡N), and 72.49 ($C(CN)_2$) ppm, as compared to those measured for K_2(*i*-mnt): 221.761, 122.955, and 72.047 ppm, respectively. Without considering the phenyl ring carbon atoms of the dppmSe ligand, $^{13}CH_2$ in dppmSe is centred at 34.33 ppm as two doublets.

^{1}H NMR shifts of the PBu^n_3 group in complex (**2**) appear at δ 0.936 (triplet), 0.980 (multiplet), and 1.487 (triplet) ppm, and ^{31}P NMR showed a singlet at 11.552 ppm. The ^{1}H NMR of the PPh_3 group in complex (**3**) showed a multiplet around 7.26–7.46 ppm for the phenyl protons and two ^{31}P signals at 32.922 and 11.047 ppm indicating the non-equivalence of the phosphine groups. The difference of the two phosphine groups is evidenced by the fact that the structural data for (**3**) showed one of the Ni-P bonds being longer than the other by some 0.03 Å.[9]

IR and electronic data for the Ni(II) complexes are listed in Table IX, together with relevant bands for K_2(*i*-mnt)[22] and K_2Ni(*i*-mnt).[23] It is seen that characteristic absorptions in the three complexes (**1**), (**3**), and (**4**) for both C≡N and C=C of *i*-mnt are red shifted by 20 ~ 30 cm^{-1} due to weakening of the bonds after the ligand is chelated to Ni(II). The weakening of the C–S bond is even more obvious by 30–35 cm^{-1}, due to direct chelation of both sulfur atoms. This agrees well with data reported for the ternary complexes Ni(L–L)$_3$(*i*-mnt),[22] where L–L is 1,10-phenanthroline or ethylenediamine. P–C absorptions are comparable with those of the free phosphine ligands and appear as multiple bands in the range 530 ~ 460 cm^{-1}. The molecular formula of complex (**4**) is thus deduced by the similar data as for other ternary complexes as shown in Table IX.

TABLE VII Comparison of structural data of some ternary thiolato–phosphine cobalt (II) complexes

Complex[a]	*Coordination geometry*	Co–S	Co–P	C–S	*Chelate rings*					
					S–Co–X X = S,N	P–Co–P	Co–S–C	Co–P–C	S–C–X X = S,N	*Ref.*
$[Co(i\text{-mnt})_2(PBu^n_3)_2]^-$	Octahedron	2.275	2.319	1.70	76.25	c	86.2	c	111.3	this work
$Co(N\text{-mbt})_2(PBu^n_3)_2$	Square plane	/	2.312	1.684[b]	c	c	c	c	c	5
$Co(N,S\text{-mbt})_2(dppe)$	Octahedron	2.711	2.234	1.687[b]	65.5	85.0	70.1	107.5	120.7	5
Co(bdt)(dppe)	Square plane	2.157	2.167	1.741	92.4	86.2	104.0	108.0	92.4	11
$[Co(bdt)_2(PBu^n_3)]^-$	Square pyramid	2.191	2.124	1.758	89.43	c	d	c	c	21

[a] mbt = 2-mercaptobenzothiazole, bdt = 1,2-benzenedithiolate. [b] S is the exocyclic sulfur when applicable. [c] Not applicable. [d] Not reported.

TABLE VIII NMR data for Ni(*i*–mnt)(dppmSe) (**1**) in DMSO–d_6 as compared to dppmSe

^1H	CH_2, ppm	C_6H_5, ppm	$^2J_{Pep-H}$[a], Hz	$^2J_{PSe-H}$[a], Hz
Complex (**1**)	5.10(t)	7.2–7.9(m)	9.0	11.5
dppmSe	3.44(dd)	6.9–7.9(m)	2.0	12.7
^{31}P	P_{ep}, ppm	P_{Se}, ppm	$^1J_{P-Se}$, Hz	$^2J_{P-P}$, Hz
Complex (**1**)	44.58(d)	43.28(d)	526	69
dppmSe	−27.2(d)	30.7(d)	730	85
^{13}C	$C(S)_2$[b], ppm	$C{\equiv}N$[b], ppm	$C(CN)_2$[b], ppm	C_P[b], ppm
Complex (**1**)	205.65(s)	113.85(s) 115.52(s)	72.49(s)	34.44(dd)
K_2(*i*–mnt)	221.761	122.955	72.047	
dppmSe				30.4(dd)

[a] P_{ep} indicates the phosphorus atom with an electron pair. P_{Se} indicates the one connected to the Se atom.
[b] Carbon atoms with S, C, N, and P indicate the atoms bonded to sulfur, carbon, nitrogen, and phosphorus atoms, respectively.

TABLE IX Characteristic IR and electronic data for the Ni(II) complexes

Complex	ν, cm^{-1}				λ, nm		*Ref.*
	C≡N	*C=C*	*C–S*	*P–C*	*Ligand*	*LMCT*	
K_2(*i*-mnt)	2181 2195	1360 1370	860 870	/ /			22 23
K_2Ni(*i*-mnt)$_2$	2215	1380	900	/			23
Ni(*i*-mnt)(dppmSe)	2208	1387	897	534 511 488 476 432	268 336 371	452	this work
Ni(*i*-mnt)(PPh_3)$_2$	2208	1380	889	521 511 494 438	270 338	455	this work
Ni(*i*-mnt)(PBu^n_3)$_2$	2210	1379	894	475 455	268 314 358	450	this work

Supplementary Material

Complete lists of bond distances, bond angles, thermal parameters, and observed and calculated structure factors for (**1**) and (**2**) are available upon request from the authors.

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References

[1] B.S. Kang, Z.N. Chen, Z.Y. Zhou, H.Q. Liu, H.R. Gao, B.M. Wu, T.C.W. Mak, Y.B. Cai, Y.J. Xu and Z.T. Xu, *J. Cluster Sci.*, **7**, 317 (1996).

[2] (a) B.S. Kang, J.H. Peng, M.C. Hong and D.X. Wu, *J. Chem. Soc., Dalton Trans.*, 2897 (1991); (b) Y.J. Xu, B.S. Kang, X.T. Chen and Y.H. Hu, *Chin. Chem. Lett.*, **3**, 1017 (1992); (c) B.S. Kang, Y.J. Xu, D.X. Wu, J.H. Peng, M.C. Hong, L.H. Weng, X.T. Chen and H.Q. Liu, *Sci. in China B*, **23**, 132 (1993); (Eng) **B36**, 912; (d) H.R. Gao, T.C.W. Mak, B.S. Kang, B.M. Wu, Y.J. Xu, Y.X. Tong and X.L. Yu, *J. Chem. Research* (*S*), 186 (1996); (e) F.L. Jiang, X.L. Xie, M.C. Hong, B.S. Kang, R. Cao, D.X. Wu and H.Q. Liu, *J. Chem. Soc., Dalton Trans.*, 1447 (1995); (f) Z.N. Chen, B.S. Kang, Z. Lin, C.N. Chen, Q.T. Liu, B.M. Wu, Z.Y. Zhou and T.C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 177 (1996).

[3] (a) Y.J. Xu, B.S. Kang, X.T. Chen, Y.B. Cai, Y.H. Hu and J.X. Lu, *J. Cluster Sci.*, **3**, 167 (1992); (b) B.S. Kang, Y.J. Xu, X.L. Xie, C.N. Chen, Q.T. Liu, H.Q. Liu and J.X. Lu, *Inorg. Chem.*, **33**, 3770 (1994); (c) F.L. Jiang, Z.Y. Huang, D.X. Wu, B.S. Kang, M.C. Hong and H.Q. Liu, *Inorg. Chem.*, **32**, 4971 (1993).

[4] Z.N. Chen, W.J. Li, B.S. Kang, M.C. Hong, Z.Y. Zhou, T.C.W. Mak, Z. Lin, X.M. Chen and H.Q. Liu, *Inorg. Chem.*, **36**, 208 (1997).

[5] B.S. Kang, H.R. Gao, Z.N. Chen, Y.X. Tong, H.Q. Liu, B.M. Wu and T.C.W. Mak, *Polyhedron*, **16**, 1731 (1997).

[6] (a) C.W. Liu, C.J. MeNeal and J.P. Fackler Jr., *J. Cluster Sci.*, **7**, 385 and references cited therein (1996). (b) S. Narula, R. Mehra, D. Winge and I. Armitage, *J. Am. Chem. Soc.*, **113**, 9354 (1991).

[7] L.E. McCandlish, E.C. Bissel, D. Coucouvanis, J.P. Fackler Jr. and K.J. Knox, *J. Am. Chem. Soc.*, **90**, 7357 (1968).

[8] K.A. Jensen and L. Henriksen, *Acta Chem. Scand.*, **22**, 1107 (1968).

[9] Z.X. Huang, S.F. Lu, J.Q. Huang and J.L. Huang, *Chin. Chem. Lett.*, **3**, 1023 (1992).

[10] *MolEN, an Interactive Structure Solution Procedure* (Enraf-Nonius, Delft, The Netherlands, 1990).

[11] B.S. Kang, Z.N. Chen, H.R. Gao, Z.Y. Zhou, B.M. Wu, T.C. W. Mak and Z. Lin, *Acta Chim. Sinica*, **56**, 58 (1998).

[12] D. Coucouvanis, N.C. Baenziger and S.M. Johnson, *Inorg. Chem.*, **13**, 1191 (1974).

[13] A.M. Bond, R. Colton and P. Panagiotidou, *Organometallics*, **7**, 1767 (1988).

[14] S.O. Grim and E.D. Walton, *Inorg. Chem.*, **19**, 1982 (1980).

[15] R. Akilan, K. Kivakumar, V. Venkatachalam, K. Ramalingam, K. Chinnakali and H.-K. Fun, *Acta Cryst.*, **C51**, 368 (1995).

[16] R. Cao, *Doctor of Science Thesis*, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (1993).

[17] K. Matsumoto, N. Saiga, S. Tanaka and S. Ooi, *J. Chem. Soc., Dalton Trans.*, 1265 (1991).

[18] M.K. Singh, R.C. Aggarwal and B. Singh, *Synth. React. Inorg. Met. -Org. Chem.*, **15**, 459 (1985).

[19] R.M. Davila, A. Elduque, R.J. Staples, M. Harlass and J.P. Fackler Jr., *Inorg. Chim. Acta*, **217**, 45 (1994).

[20] H. Dietrich, W. Storck and G. Manecke, *J. Chem. Soc., Chem. Commun.*, 1036 (1982).

[21] B.S. Kang, J.H. Peng, M.C. Hong, D.X. Wu, X.T. Chen, L.H. Weng, X.J. Lei and H.Q. Liu, *J. Chem. Soc., Dalton Trans.*, 2897 (1991).

[22] M.K. Singh, *Indian J. Chem.*, **30A**, 1070 (1991).

[23] J.P. Fackler Jr. and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).